UTILITY PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Alexander S. KOZLOV
Group Art Unit: 1753
Serial No.: 10/753,675
Examiner: H. D. Wilkins III
Filed: January 7, 2004
Confirmation No.: 1132
For: PLATINUM ALUMINIDE COATING AND METHOD THEREOF
Docket No.: H0005756
Customer No.: 000128

RENEWED PETITION UNDER 37 C.F.R. §1.47

Office of Petitions
EXAMINER Paul SHANOSKI
Washington, D.C. 22031

Commissioner:

In accordance with the provisions of 37 C.F.R. 1.47(a), applicants Derek Raybould, Siu-Ching Lui, and Thomas E. Strangman, through their attorney, hereby renew their petition to file the above identified application without the Declaration of joint inventor Mr. Alexander S. Kozlov on account of Mr. Kozlov's being deceased and the unavailability of any of his surviving heirs to execute a Declaration in the application.

This renewed petition responds to a Decision on Petition mailed on August 14, 2008 ("Decision") in which an original petition filed on June 18, 2008 ("Original Petition") was allegedly defective. In particular, the Decision alleges that a complete copy of the application was not sent to the last-known address of the legal representative and that the declaration that was submitted on initial deposition failed to contain the name of the legal representative, state the she is a legal representative and list her citizenship, residence, and mailing address. This renewed petition is accompanied by papers that correct the alleged defects of the Original Decision. In particular, a complete copy of the application and a corrected Declaration were sent to the last-known address of the legal representative. Additionally, the corrected Declaration contained the legal representative's name, a

statement that the legal representative was a legal representative, and a listing of the legal representative's citizenship, residence, and mailing address

New declarations setting out the pertinent facts in accordance with the provision of Rule 1.47(a) are enclosed herewith.

As set forth in the enclosed declarations, diligent attempts were made to deliver a package containing a copy of the specification, claims, drawings, and an oath for signature related to the above identified application Svetlana Kozlova, the last known sole surviving heir of Mr. Kozlov, directly at her last known address. However, the package was not deliverable to Ms. Kozlova, as she was not locatable.

Ms. Kozlova's last known address, as set forth on the declaration, is

Golubinskaja 7, Korp 5 KV. 260
Moscow 117574, Russia

A Declaration of Missy Hale and a Declaration of Cindy H. Kwacala, both of whom have first-hand knowledge of the diligent efforts and failure to obtain the Declaration of sole surviving heir Svetlana Kozlova of joint inventor Alexander S. Kozlov, are submitted herewith.

Favorable consideration of the present petition is respectfully requested.

Respectfully submitted,
INGRASSIA FISHER & LORENZ

Dated: October 14, 2008

By: /CINDY H. KWACALA/
Cindy H. Kwacala
Reg. No. 47,667

UTILITY PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Alexander S. KOZLOV
Serial No.: 10/753,675
Filed: January 9, 2004
For: PLATINUM ALUMINIDE COATING AND METHOD THEREOF
Docket No.: H0003756

Group Art Unit: 1753
Examiner: H. D. Wilkins III
Confirmation No.: 1132

DECLARATION OF CINDY H. KWACALA

I, Cindy H. Kwacala, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1000 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application and of any patent issuing therefrom.

1) I am a patent attorney for the law firm of Ingrassia, Fisher & Lorenz, 7010 East Cochise Road, Scottsdale, Arizona 85253 ("IF&L") which acts as outside counsel for client Honeywell International, Inc. of Law Dept. AB2, P.O. Box 2245, Morristown, New Jersey 07962-9806 ("Honeywell"). Part of my responsibility is to prosecute patent applications that have been filed and prepared by other Honeywell outside counsel and subsequently transferred to IF&L and to work with our patent paralegals to obtain signatures of Honeywell inventors on Combined Declaration and Power of Attorneys and Assignments for Honeywell patent applications.

2) On August 14, 2008, the United States Patent and Trademark Office ("USPTO") mailed a Decision of Petition requiring re-submission of an executed declaration for the above-referenced application.

3) On September 6, 2008, I instructed IF&L paralegal Missy Hale to send a package via Federal Express ("Federal Express package") to deceased inventor Alexander S. Kozlov's sole surviving heir, Svetlana Kozlova at Ms. Kozlova's last known address:

Golubinskaja 7, Korp 5 KV. 260
Moscow 117574, Russia

The Federal Express package included a copy of the Combined Declaration and Power of Attorney, a copy of the Assignment, a letter in English to Ms. Kozlova requesting her signatures on the declaration and the assignment, a letter translated into Russian to Ms. Kozlova requesting her signatures on the declaration and the assignment, a copy of the specification, claims, and drawings of the above-referenced application, a self-addressed stamped Federal Express envelope to return the signed documents back to IF&L, and a listing of the package contents. A copy of the contents of the Federal Express package is attached.

4) On September 16, 2008, I received a call from Federal Express indicating that a delivery person from Federal Express attempted several deliveries of the Federal Express package to Ms. Kozlova, but that the delivery person was unable to locate Ms. Kozlova.

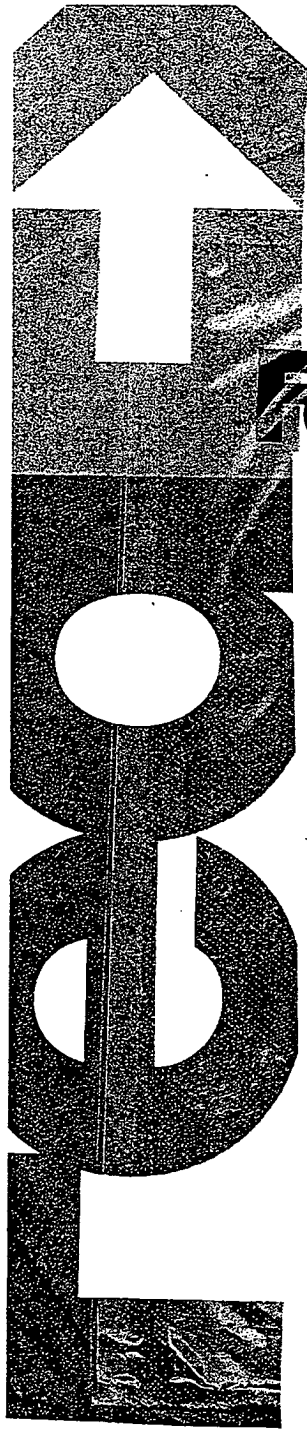
5) On September 17, 2008, Ms. Hale forwarded an email to me from Federal Express indicating that the Federal Express package had been undeliverable. A copy of the email is attached.

6) To date, IF&L has not received a returned signed copy of the Combined Declaration and Power of Attorney or the Assignment.

7) I am left to conclude that sole surviving heir Ms. Svetlana Kozlova of joint inventor Alexander S. Kozlov is unavailable to sign the Combined Declaration and Power of Attorney and Assignment papers.

Date: October 14, 2008

Cindy H. Kwaczala



FedEx Express

Page 2 of 2

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7010 E. Cochise Road

SCOTTSDALE, AZ 85253
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DESC-2:
DESC-3:
DESC-4:
EEI: NO EEI 30.37(a)
COUNTRY MFG: US
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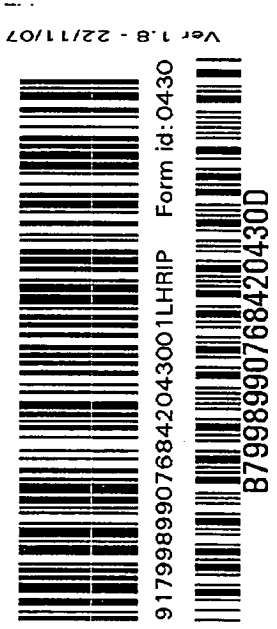

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• Admitted to practice in AZ

Patent Agent
David P. Manelli

VIA FEDERAL EXPRESSS

September 2, 2008

Svetlana Kozlova
Golubinskaja 7, Korp 5 KV. 260
Moscow 117574, Russia

Re: Alexander S. Kozlov
Our ref no.: H0005756

Dear Ms. Kozlova:

Our law firm represents Honeywell International Inc., the former employer of Alexander Kozlov. We understand that you are the daughter of Mr. Kozlov who resided in New Jersey, United States of America, and that you previously signed and returned documents relating to a patent on which he was an inventor.

To comply with a request from the United States Patent and Trademark Office, we need to obtain another signed version of the documents that you previously signed. Thus, I would greatly appreciate it if you would please re-sign the documents and send them to us by September 26, 2008. The documents are attached to this letter. If we do not receive the signed documents by September 26, we will need to file a Petition stating that we could not reach you.

Because the deadline is approaching, please fax the signed documents to us at (480) 385 0 61, and please return the original version using the mail system. For your convenience, we ·ve included a self-addressed, postage-prepaid envelope in which you may return the original ·sion of the signed documents.

Finally, please let me know if you would like a copy of your father's patent, and I will be glad to send it to you. Thank you for your assistance.

Very truly yours,

INGRASSIA FISHER & LORENZ, P.C.

Cindy H. Kwacala

Cindy H. Kwacala

List of documents included in envelope

Letter (English version)
Copy of letter (Russian version)
Declaration
Assignment
Patent Application and drawings
Self-Address Pre-paid Return Federal Express Envelope

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Patent Agent
David P. Mancini

ЗАКАЗНОЙ ПОЧТОЙ
С ПОДПИСЬЮ АДРЕСАТА О ПОЛУЧЕНИИ

2 сентября 2008г.

Россия, Москва- 117574,
ул. Голубинская, 7, корп. 5, кв. 260,
г-же Светлане Козловой

Кас.: Александр С. Козлов
Наш спр. №: H0005756

Уважаемая г-жа Козлова!

Наша юридическая фирма представляет компанию Honeywell International Inc., где в прошлом работал Александр Козлов. Насколько нам известно, Вы являетесь дочерью г-на Козлова, который проживал в Нью Джерси, Соединенные Штаты Америки, и в прошлом Вы подписали и вернули документы, связанные с патентом, изобретателем которого он является.

В соответствии с запросом Офиса по делам патентов и торговых знаков Соединенных Штатов нам нужно получить еще один экземпляр документов, которые Вы ранее уже подписали. Поэтому я буду благодарна, если Вы еще раз подпишете документы и отправите их нам до 26 сентября 2008г. Документы приложены к этому письму. Если мы не получим подписанные Вами документы до 26 сентября, нам придется подать заявление и указать, что мы не могли с Вами связаться.

Поскольку времени до указанного срока остается мало, отправьте, пожалуйста, подписанные документы по факсу (480) 385 50 61 и верните, пожалуйста, оригинал по почте. Для удобства мы прилагаем оплаченный и адресованный конверт, в котором Вы можете отправить оригинал подписанных документов.

Сообщите мне, пожалуйста, нужна ли Вам копия патента Вашего отца, я буду рада отправить ее Вам. Благодарю Вас за помощь.

С уважением,

INGRASSIA FISHER & LORENZ, P.C.

Cindy H Kvacala /n

Синди Х. Квакала

United States Patent Application
Attorney Docket No.: H0005756
First Named Inventor: Alexander S. Kozlov

ASSIGNMENT

WHEREAS, the undersigned inventor(s) (hereinafter individually and collectively referred to as "ASSIGNOR") has/have invented:

PLATINUM ALUMINIDE COATING AND METHOD THEREOF

(hereinafter, "the invention") for which application for Letters Patent of the United States:

[ ] has been executed on even date herewith;

[ ] was executed on _____;

[X] was filed on January 7, 2004 and assigned U.S. application serial no. 10/753,675;

AND WHEREAS, Honeywell International Inc., a Delaware corporation having a place of business at 101 Columbia Road, POB 2245, Morristown, N.J. 07962-2245 (hereinafter "ASSIGNEE"), and its successors, assigns, and legal representatives, is desirous of acquiring, and the ASSIGNOR is desirous of assigning and transferring the entire right, title, and interest therein;

AND WHEREAS, a "formal application," as referred to herein, shall mean any provisional, nonprovisional, continuation, continuation in part, continued prosecution, substitute, renewal, extension, divisional, reissue, reexamination, foreign, Patent Cooperation Treaty (PCT) or other patent application, inventor's certificate, utility model, or like document;

NOW, THEREFORE, for good and valuable consideration, the receipt and sufficiency of which are hereby acknowledged, ASSIGNOR does hereby irrevocably and unconditionally assign and transfer unto ASSIGNEE, its successors, assigns, and legal representatives, the entire right, title and interest in and to the aforesaid application, to the invention as described in the aforesaid application, and to any formal application which may be filed based in whole or in part on the aforesaid application, in the United States and all foreign countries, together with the right of priority under any international conventions, treaties and/or agreements to which the United States currently adheres and adheres to in the future and with all ancillary rights thereto, including the right to sue and recover for, and the right to profits or damages due or accrued, arising our of or in connection with, any and all past, present or future infringements of any such rights, and hereby authorizes and requests the Commissioner of Patents to issue said Letters Patent to ASSIGNEE, for the sole use and benefit of ASSIGNEE, its successors, assigns, and legal representatives;

AND ASSIGNOR authorizes ASSIGNEE, its successors, assigns, and legal representatives, or anyone it may properly designate, to apply for Letters Patent, in its own name if desired, in any and all foreign countries, and additionally to claim the filing date of aforesaid application and/or otherwise take advantage of the provisions of any international convention, treaty and/or agreement;

AND ASSIGNOR FURTHERMORE authorizes ASSIGNEE, its successors, assigns, and legal representatives, or anyone it may properly designate, to insert in this instrument the filing date and/or serial number of said application when ascertained;

AND ASSIGNOR HEREBY AGREES to transfer, upon request of ASSIGNEE, its successors, assigns, and legal representatives, and without further remuneration, a like interest in and to any related inventions and formal applications based thereon;

AND ASSIGNOR AGREEING, FURTHERMORE, upon request of ASSIGNEE, and without further remuneration, but at no expense to ASSIGNOR, that ASSIGNOR will provide all reasonable assistance to obtain, maintain, and assert the fullest measure of legal protection that ASSIGNEE desires to obtain or assert for the invention, any related inventions, any formal application based thereon, and any resulting patents, including executing any and all papers desired by ASSIGNEE for the filing and granting of formal applications, the perfecting of title in ASSIGNEE, and in enforcing any rights in the invention, any related inventions, and any formal application or patent based thereon.

This instrument is executed by, an shall be binding upon, ASSIGNOR, his heirs, executors and administrators, for the uses and purposes above set forth and referred to and shall inure to the benefit of ASSIGNEE, its successors, assigns and legal representatives, or anyone it may properly designate.

If any provision of this assignment is held by any court to be unenforceable, such provision shall be interpreted to accomplish the objectives of the original provision to the fullest extent allowed by law and the remainder of this assignment shall remain in full force and effect.

EXECUTED as of the date(s) written below by ASSIGNOR:

_____ Date: _____

Alexander S. Kozlov, deceased and being represented by legal representative Svetlana Kozlova

_____ Date: _____

Derek Raybould

_____ Date: _____

Siu-Ching D. Lui

_____ Date: _____

Thomas E. Strangman

"Express Mail" label number EV374985827US

Date of deposit _____

I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to: MAIL STOP PATENT APPLICATION, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Michael A. Shimokaji, Reg. No. 32,303

PATENT
H0005756-1060

PLATINUM ALUMINIDE COATING AND METHOD THEREOF

BACKGROUND OF THE INVENTION

[0001] The present invention generally relates to co-electrodeposition of platinum and a supplementary constituent to platinum aluminide coatings, and to methods for forming such coatings.

[0002] In modern gas turbine engines, the blades and vanes in the high pressure turbine section are exposed to temperatures in excess of 1000° C for extended periods of time. Superalloy gas turbine engine components are commonly coated with platinum aluminide coatings to inhibit oxidation and corrosion of the superalloy surface. Protection provided by platinum aluminide coatings is due to selective oxidation of aluminum to form an alumina (Al_2O_3) scale that grows very slowly at high temperature by a diffusion process.

[0003] Impurities within the platinum aluminide coating, e.g., sulfur (S), phosphorus (P), and chlorine (Cl), can segregate to the interface between the coating and the alumina scale, weaken the interface, and thus promote spalling of the protective oxide scale. Periodic oxide spalling accelerates the consumption of aluminum from the platinum aluminide coating and reduces the oxidation life of the component. Impurity-induced oxide spalling of the protective oxide scale also limits the life of thermal barrier coatings that utilize platinum aluminide coatings as a bond coating.

[0004] U.S. Patent No. 6,306,277 to Strangman *et al.* discloses an electroplating process for electrodeposition of platinum on superalloy substrates, and a platinum electrolyte for use in such electroplating process, wherein the electrolyte is stable and readily prepared. The electrolyte

comprises the platinum salt, dinitrodiamine platinum ($Pt(NH_3)_2(NO_2)_2$), and an alkali metal carbonate or bicarbonate; and the process results in decreased contaminant levels of S, Cl, and P in the electroplated Pt layer, as compared with Pt layers deposited using prior art electrolytes.

[0005] It is known that the presence of chromium (Cr) in superalloy coatings (e.g., Cr containing platinum aluminide coatings) increases the corrosion resistance of superalloy components, and hence increases the life of such components, as compared with platinum aluminide coatings which substantially lack Cr.

[0006] EP 0821076 A1 to Wing discloses a process for forming a platinum aluminized chromised Ni-based superalloy, wherein the process involves the steps of: 1. forming a chromium enriched surface layer of the superalloy, e.g., by electroplating; 2. heating in a vacuum or protective atmosphere; 3. forming a platinum layer on the chromium enriched superalloy by electroplating, sputtering, etc.; 4. heating in a vacuum or protective atmosphere for one to four hours at 900° to 1150° C; and 5. aluminizing the chromised, diffused, platinum coated Ni-based superalloy, e.g., by out of pack aluminizing for six hours at 1080° C. Thus, in the process of Wing, Cr and Pt are deposited on the superalloy in separate steps.

[0007] U.S. Patent No. 5,482,578 to Rose *et al.* discloses a diffusion coating process for the deposition of a coating of chromium-containing $PtAl_2$ on a superalloy substrate. The process of the '578 patent involves: 1. deposition of a platinum group metal on the superalloy, e.g., by electroplating; 2. heating *in vacuo* at about 1900° F for about an hour; 3. diffusion coating the platinum-group metallized superalloy with an Al/Cr powder; and finally 4. heat treating the Al/Cr diffusion coated, metallized superalloy at about 1925° to 2050° F in hydrogen for about one to two hours. Again, in the process of Rose, *et al.*, Cr and Pt are deposited on the superalloy in separate steps.

[0008] As can be seen, there is a need for a process for concurrently depositing platinum and a supplementary constituent on a substrate in a single

step. There is a further need for a readily applied Cr containing platinum aluminide coating for superalloy gas turbine engine components. There is a further need for a process for coating superalloy components with a Cr containing platinum aluminide coating, wherein Pt and Cr are deposited on the superalloy surface in a single electrolytic step, such that processing costs are decreased, and productivity is increased. There is also a need for a reliable, stable, effective, and readily available electrolyte composition for co-electrodeposition of Pt and Cr on a substrate.

SUMMARY OF THE INVENTION

[0009] In one aspect of the present invention, there is provided a method for electroplating platinum, including providing a substrate, and electrolytically depositing a metal layer on a surface of the substrate. The metal layer comprises platinum and a supplementary constituent, and the metal layer is deposited from a single electrolyte composition during a single electrolytic step. The electrolyte composition comprises a platinum salt and particles of the supplementary constituent, and the particles of the supplementary constituent are deposited in the metal layer from the electrolyte composition.

[0010] In another aspect of the present invention, there is provided a method for electroplating platinum on a substrate, including electroplating platinum metal on the substrate via an electrolyte comprising particles of one or more supplementary constituents; and, concurrently with electroplating the platinum metal, depositing particles of the one or more supplementary constituents on the substrate. Beneficial supplementary constituents may comprise the following elements, which may be selected for their ability to form protective oxides (Al, Cr), enhance adhesion of protective oxides (Y, Zr, Hf, La, Sc, Si), enhance coating ductility (Ni, Co), enhance coating strength at high temperatures (Ta, Re), and reduce the diffusional interaction with the substrate (Ni, Co, Fe).

[0011] In still another aspect of the present invention, there is provided a process for preparing a coated component, including providing a substrate; electroplating a metal layer on a surface of the substrate, wherein the electroplated metal layer comprises platinum metal and particles of at least one supplementary constituent entrapped within the platinum metal; depositing aluminum on the electroplated metal layer; and forming a platinum aluminide coating on the substrate, wherein the platinum aluminide coating comprises the supplementary constituent. Elements present in the substrate, such as nickel, may be incorporated into the coating during a high-temperature post-plating diffusion heat treatment, high-temperature diffusion aluminizing processing, or post-aluminizing heat treatments. Major elements present within the coating may be Pt, Ni (from the substrate) and Al. Major constituent elements are predominately present in the form of intermetallic phases following aluminizing and heat treatment. In particular, the NiAl phase has solubility for Pt and other elements. Even though Ni may be a major constituent of the coating composition on a Ni-based substrate, the coatings are known in the industry as Pt-aluminides, which refers to the elements that are added during coating processing. We also use the industrial terminology for these coatings.

[0012] In yet another aspect of the present invention, a process for preparing a coated component may include providing a substrate; electroplating a platinum metal layer on the substrate, wherein the platinum metal layer is electrodeposited via an electrolyte composition comprising chromium particles; concurrently with electroplating the platinum metal layer, depositing the chromium particles on the substrate, wherein the chromium particles are entrapped within the platinum metal layer. The process may further include exposing the substrate to a first heat treatment; thereafter, aluminizing the substrate; and exposing the substrate to a second heat treatment to form a platinum aluminide coating on the substrate, wherein the coating comprises a solid solution of chromium within the intermetallic phase comprising Pt and Al. Particles of elemental Cr or Cr-carbides may also be dispersed within the

coating microstructure. Carbon to form a carbide within the coating may be the result of a coating diffusion reaction with a carbon-containing substrate.

[0013] In an additional aspect of the present invention, there is provided a component including a metal substrate, and a platinum aluminide coating disposed on the substrate. The platinum aluminide coating comprises platinum and chromium, wherein the chromium is co-electrodeposited with the platinum, wherein the chromium forms a solid solution within the platinum, and the coating is free from, or substantially free from, chlorine, sulfur, phosphorus, or compounds thereof.

[0014] In a further aspect of the present invention, there is provided a corrosion- and oxidation resistant coating, comprising electrodeposited platinum, and chromium. The chromium is co-electrodeposited with the platinum, the chromium forms a solid solution within the platinum and substrate elements, such as Ni, Co, or Fe, and the coating is free from, or substantially free from, chlorine, sulfur, phosphorus, or compounds thereof.

[0015] In another aspect of the present invention, an electrolyte composition for electrodeposition of platinum comprises a platinum salt, a carbonate or bicarbonate of an alkali metal, and particles of at least one supplementary constituent such as Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

[0016] In yet another aspect of the present invention, an electrolyte composition for electrodeposition of platinum comprises dinitrodiamine platinum, an alkali metal carbonate or bicarbonate, and from about 0.2 to 80 g/L of chromium metal powder.

[0017] These and other features, aspects and advantages of the present invention will become better understood with reference to the following drawings, description and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figure 1A is a sectional view schematically representing a component having a corrosion- and oxidation resistant coating, according to one embodiment of the invention;

[0019] Figure 1B is a sectional view schematically representing a component having a platinum aluminide coating disposed on a substrate, and an additional layer disposed on the platinum aluminide coating, according to another embodiment of the invention;

[0020] Figure 2 schematically represents a series of steps involved in a method for electroplating platinum and a supplementary constituent on a substrate, according to one embodiment of the invention;

[0021] Figure 3 schematically represents a series of steps involved in a method for forming a corrosion- and oxidation resistant coating on a substrate, according to another embodiment of the invention;

[0022] Figure 4 schematically represents a series of steps involved in a method for coating a component, according to the invention;

[0023] Figures 5A-D schematically represent stages in preparing a corrosion- and oxidation protective coating, according to another embodiment of the invention;

[0024] Figure 6A is a scanning electron micrograph of an electroplated chromium containing platinum metal layer on a nickel substrate, according to another embodiment of the invention;

[0025] Figure 6B is an energy-dispersive x-ray spectrum taken from the image area of Figure 6A;

[0026] Figure 7A is a scanning electron micrograph of an electroplated chromium containing platinum metal layer showing a chromium particle entrapped within the electroplated layer, also according to the invention;

[0027] Figure 7B is an energy-dispersive x-ray spectrum taken from the chromium particle shown in Figure 7A, according to the invention;

[0028] Figure 8A is a scanning electron micrograph of an annealed electroplated chromium containing platinum metal layer, also according to the

invention; and

[0029] Figure 8B is an energy-dispersive x-ray line-scan corresponding to the profile of the image area of Figure 8A.

DETAILED DESCRIPTION OF THE INVENTION

[0030] The following detailed description is of the best currently contemplated modes of carrying out the invention. The description is not to be taken in a limiting sense, but is made merely for the purpose of illustrating the general principles of the invention, since the scope of the invention is best defined by the appended claims.

[0031] Broadly, the present invention provides corrosion- and oxidation resistant chromium- and/or reactive element-containing platinum aluminide protective coatings for substrates that are prone to corrosion and oxidation and, in particular, for substrates that are exposed to high temperatures in the range of 600 to 1150°C during service conditions. The reactive element may be a metal such as Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Protective coatings of the instant invention may be applied to a broad range of substrates, including substrates comprising iron-, nickel-, and cobalt-based alloys, such as nickel-based superalloys. Protective coatings of the instant invention may be used in a diverse array of industrial applications where corrosion and oxidation protection of components or substrates is required, including: gas turbine engines used for aircraft propulsion, automotive power, and power generation, as well as chemical processing.

[0032] As a specific example, coatings of the instant invention may be used to protect components such as blades and vanes in the high pressure turbine section of gas turbine engines. Platinum aluminide coatings of the present invention may serve as a stand-alone protective coating. Platinum aluminide coatings of the present invention may also function as a bond coating for deposition of an additional layer, such as a ceramic thermal barrier coating,

directly on the bond coating.

[0033] In general, platinum alloy protective coatings of the instant invention may be formed by a platinum electrodeposition process involving the concurrent electrodeposition of platinum and powder containing one or more supplementary constituents, such as chromium, chromium oxide, a chromium alloy, a reactive element, or an alloy of a reactive element, from a single electrolyte composition to form an electrodeposited metal layer on a substrate to be coated. Pt-aluminide coatings of the instant invention may be formed by subsequent aluminizing the platinum alloy coating and heat treatment.

[0034] In contrast, in prior art platinum aluminide coating processes, platinum and chromium have been deposited in separate steps. As an example, a prior art process for deposition of Pt and Cr disclosed in US Patent No. 5,482,578 involves deposition of a platinum group metal on the superalloy, heating *in vacuo* at about 1900° F for about an hour, diffusion coating the platinum-group metallized superalloy with an Al/Cr powder, and finally heat treating the Al/Cr diffusion coated, metallized superalloy at about 1925° to 2050° F in hydrogen for about one to two hours.

[0035] In further contrast to the prior art, and in one embodiment of the present invention, chromium and platinum constituents of a Cr containing platinum aluminide coating may be electrolytically co-deposited on a substrate surface, in a single step, using an electrolyte composition comprising a platinum salt and Cr metal powder.

[0036] An electrolyte composition of the instant invention may be free from, or substantially free from, sulfur, chlorine, and phosphorus impurities. Moreover, a platinum aluminide coating prepared using such an electrolyte composition may similarly be free from, or substantially free from, sulfur, chlorine, and phosphorus impurities. In contrast, electrolyte compositions used in prior art platinum aluminide coating processes result in the co-deposition of sulfur, chlorine, and phosphorus impurities in the electroplated platinum metal layer. The presence of sulfur, chlorine, and phosphorus impurities reduces the

life of the coating and of the coated component.

[0037] An electrolyte for electroplating superalloy components previously disclosed in commonly assigned US Patent No. 6,306,277 contained the platinum salt, dinitrodiamine platinum, and was substantially free from sulfur, chlorine, and phosphorus impurities. However, in contrast to the instant invention, the electrolyte of the '277 was not described as containing metal particles or chromium.

[0038] Figure 1A is a sectional view schematically representing a component 200, according to one embodiment of the invention. Component 200 may include a substrate 202 and a coating 210 disposed on substrate 202. Coating 210 may be a corrosion resistant protective coating. Coating 210 may also be an oxidation resistant protective coating. Coating 210 may be a stand-alone corrosion- or oxidation resistant coating. Coating 210 may also serve as a bond coating adapted for accepting an additional coating thereon (see, for example, Figure 1B).

[0039] Again with reference to Figure 1A, coating 210 may be a platinum aluminide coating. For example, coating 210 may comprise platinum and aluminum in an intermetallic compound. Coating 210 may further comprise at least one supplementary constituent. The at least one supplementary constituent may include a metal, such as chromium, or an oxide such as chromium oxide, both of which may impart the characteristic of corrosion resistance to coating 210. The at least one supplementary constituent may additionally, or alternatively, include one or more reactive elements, such as Al, Cr, Y, Zr Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. The one or more reactive elements may impart the characteristic of oxidation resistance to coating 210. The one or more reactive elements may further impart, to some extent, the characteristic of corrosion resistance to coating 210. Similarly, the presence of chromium may impart, to some extent, the characteristic of oxidation resistance as well as corrosion resistance to coating 210. The one or more reactive elements may further impart, to some extent, the characteristic of ductility to

coating 210. The one or more reactive elements may further impart, to some extent, the characteristic of high-temperature strength, or resistance to stress-relaxation, to coating 210.

[0040] In some embodiments, the at least one supplementary constituent may comprise a powdered chromium alloy, such as an alloy of chromium with at least one of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Coating 210 may comprise platinum metal and a solid solution of at least one supplementary constituent. For example, after a post-plating heat treatment, coating 210 may be a solid-solution alloy comprising platinum, chromium, and the base-metal. The supplementary constituent, e.g., chromium, may be substantially uniformly distributed within coating 210. The platinum and supplementary constituent(s) of coating 210 may be electrodeposited, e.g., electroplated or electroformed, on substrate 202. As an example, the platinum of coating 210 may be electrodeposited via an electrolyte composition comprising a platinum salt and particles of at least one supplementary constituent. The chromium or other supplementary constituent of coating 210 may be co-electrodeposited with platinum. That is to say, the chromium or other supplementary constituent of coating 210 may be electrodeposited concurrently with electrodeposition of platinum from a single electrolyte composition, during a single electrolytic step.

[0041] The single electrolytic step for co-electrodeposition of chromium and platinum may provide an electroplated layer comprising platinum metal and a plurality of chromium particles entrapped therein. Herein, coatings, compositions, and processes of the invention may be described with reference to chromium, it being understood that in some embodiments other supplementary constituent(s), such as chromium oxide, various chromium alloys, or one or more reactive elements, may be used alternatively, or in addition to, chromium.

[0042] Again with reference to Figure 1A, substrate 202 may comprise an iron-, nickel-, or cobalt-base alloy. For example, the substrate may be a nickel-base superalloy. Component 200 may be a gas turbine engine component,

such as a turbine blade or vane. However, the present invention is not limited to gas turbine engine components, but rather the present invention may find applications wherever corrosion- and/or oxidation resistant coatings are required.

[0043] An electrolyte composition for concurrent deposition of platinum and chromium, according to one aspect of the invention, may comprise the platinum salt, dinitrodiamine platinum ($Pt(NH_3)_2(NO_2)_2$), in an amount typically in the range of from about 1 to 100 g/L, usually from about 5 to 75 g/L, and often from about 25 to 55 g/L.

[0044] The electrolyte composition for concurrent deposition of platinum and chromium may further comprise an alkali metal (Group I element) carbonate or bicarbonate, i.e., M_2CO_3 or $MHCO_3$, wherein M is Li, Na, K, Rb, or Cs. The alkali metal carbonate or bicarbonate may be present in an amount typically in the range of from about 1 to 200 g/L, usually from about 10 to 175 g/L, and often from about 50 to 150 g/L. The electrolyte composition may be prepared by adding the platinum salt and the alkali metal carbonate or bicarbonate to water.

[0045] The electrolyte composition for concurrent deposition of platinum and chromium may further comprise particles of at least one supplementary constituent. As an example, the electrolyte composition for concurrent deposition of platinum and chromium may comprise chromium metal powder. The particles of chromium metal powder in the electrolyte composition may have a mean diameter in the range of from about 1 to 50 microns, usually from about 1 to 20 microns, and often from about 1 to 10 microns. The electrolyte composition for the concurrent deposition of platinum and chromium may comprise particles in the range of from about 0.2 to 400 g/L, usually from about 0.2 to 50 g/L, and often from about 1 to 20 g/L. Chromium powder may be alloyed with one or more supplementary constituents. Alternatively, an electrolyte composition for concurrent deposition of platinum and one or more supplementary constituents may include particles consisting entirely of one or

more supplementary constituents other than chromium.

[0046] The electrolyte composition for concurrent deposition of platinum and chromium may be free from, or substantially free from, chlorine (Cl), sulfur (S), phosphorus (P), or compounds thereof. For example, the electrolyte composition may comprise from zero to trace quantities of sulfur, chlorine, and phosphorus. Similarly, coating 210 prepared from co-electrodeposited Pt and Cr according to the present invention may be free from, or substantially free from, chlorine (Cl), sulfur (S), phosphorus (P), or compounds thereof.

[0047] After aluminizing and heat treatment have been completed, platinum aluminide coating 210 may have a thickness in the range of from about 5 to 100 microns, typically in the range of from about 10 to 70 microns, and usually in the range of from about 20 to 50 microns.

[0048] Figure 1B is a sectional view schematically representing a component 200', according to another embodiment of the invention. Component 200' may include a substrate 202 and a coating 210' disposed on substrate 202. Coating 210' may have the same, or similar, characteristics and features as described herein for coating 210 (Figure 1A). Similarly, coating 210' may be formed using the same, or similar, processes as for forming coating 210.

[0049] Coating 210' may serve as a platinum aluminide bond coating, and component 200' may further include an additional layer 220 disposed on bond coating 210'. As an example, additional layer 220 may be a columnar, ceramic thermal barrier coating. Such a thermal barrier coating may comprise a stabilized zirconia, such as an yttria stabilized zirconia. A columnar, ceramic thermal barrier coating is disclosed in commonly assigned, co-pending U.S. Patent Application Serial No. 10/621,981, filed July 16, 2003 (entitled: *Thermal Barrier Coating with Stabilized Compliant Microstructure*), the disclosure of which is incorporated by reference herein in its entirety.

[0050] Figure 2 schematically represents a series of steps involved in a method 300 for electroplating platinum and a supplementary constituent on a

substrate, according to one embodiment of the invention. Step 302 may involve providing a substrate. The substrate may comprise iron-, nickel-, or a cobalt-base alloy. The substrate may be a nickel-based superalloy, e.g., a superalloy for a gas turbine engine component.

[0051] Step 304 may involve providing an electrolyte composition. The electrolyte composition may have characteristics and constituents as described hereinabove. For example, the electrolyte composition may include a platinum salt, an alkali metal carbonate or bicarbonate, and particles of one or more supplementary constituent(s). The supplementary constituent(s) may comprise particles in the form of a metal powder or metal oxide powder. The one or more supplementary constituents may include a corrosion resistant material, such as chromium metal, chromium oxide, and/or Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. As an example, the one or more supplementary constituents may comprise a mixture of chromium powder, or chromium oxide powder, with elemental or alloyed particles of a reactive element such Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In some embodiments, the electrolyte composition may include a supplementary constituent comprising a chromium alloy, wherein the chromium alloy comprises chromium and one or more reactive elements such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Quantitative data on the composition of an electrolyte of the instant invention are provided elsewhere herein.

[0052] Again with reference to Figure 2, step 306 may involve electrodepositing platinum metal on the substrate and, at the same time, depositing at least one supplementary constituent on the substrate surface, via the electrolyte provided in step 304. That is to say, according to the instant invention, particles of a supplementary constituent, such as chromium, chromium oxide, a reactive element, or a chromium alloy, may be electrodeposited concurrently with electrodeposition of platinum in a single electrolytic step (e.g., step 306 of method 300) from a single electrolyte composition. The reactive element may be a metal or alloy comprising Al, Cr,

Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Prior to step 306, the substrate may be prepared by grit blasting or mechanically polishing the substrate surface to be coated. The substrate may be further prepared by chemical activation, for example, by exposure to HCl.

[0053] The electrolyte composition may be agitated or sonicated prior to step 306. The electrolyte composition may be stirred during step 306. Accordingly, during step 306 particles of the one or more supplementary constituents may be maintained in suspension.

[0054] Step 306 may involve applying a voltage between the substrate (cathode) and one or more anodes. The one or more anodes may each comprise platinum. The voltage between the substrate and the one or more anodes may be in the range of from about 1.2 to 2.2 volts, usually from about 1.5 to 2.0 volts, and often from about 1.7 to 1.9 volts. The current density per unit area of the substrate may be in the range of from about 2.0 to 3.0 $A.dm^{-2}$. During step 306, the electrolyte composition may be maintained at a temperature in the range of from about 60 to 100° C, usually from about 75 to 95° C, and often from about 82 to 86° C.

[0055] In step 308, the substrate and the electrodeposited layer formed during step 306 may be heated or annealed. For example, heat may be applied to promote bonding of the electrodeposited layer to the substrate surface, or to interdiffuse constituents of the electrodeposited layer with the surface layer of the substrate.

[0056] In some embodiments, step 308 may involve performing a first heat treatment, or annealing, the substrate. The first heat treatment may be performed at a relatively low temperature sufficient to promote bonding of the electrodeposited layer to the substrate surface. A temperature in the range of from about 300 to 650° C may be sufficient to promote such bonding of the electrodeposited layer to the substrate surface. The coating after heat treatment in the above range may still consist of platinum and particles of the supplementary constituent material.

[0057] Alternatively, the heat treatment of step 308 may be performed at a relatively high temperature sufficient to promote interdiffusion of constituents of the electrodeposited layer with the adjacent surface layer of the substrate surface. A temperature in the range of from about 1000 to 1100° C may be sufficient to promote such diffusion of constituents of the electrodeposited layer and the substrate. When a heat treatment in the 1000 to 1100° C range is performed, the resulting coating may comprise a solid solution alloy; e.g., the coating may comprise a metallic solid solution of Ni, Pt and Cr when the substrate is a nickel-base alloy.

[0058] Step 308 may be performed, for a period in the range of from about 15 minutes to four (4) hours, in a protective atmosphere (e.g., in argon), or under vacuum.

[0059] Figure 3 schematically represents a series of steps involved in a method 400 for forming a corrosion- and oxidation resistant coating on a substrate, according to another embodiment of the invention. Step 402 may involve providing a substrate, generally as described hereinabove with respect to step 302, method 300 (Figure 2).

[0060] Step 404 may involve concurrently depositing platinum metal and at least one supplementary constituent on the substrate surface, via a single electrolyte composition. The electrolyte may have the composition and characteristics described hereinabove. For example, the electrolyte may comprise a platinum salt and particles of one or more supplementary constituents, such as chromium, chromium oxide, Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re, or a chromium alloy. Such an alloy of chromium may include one or more metals such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Step 404 may be performed generally as described hereinabove with respect to step 306, method 300 (Figure 2).

[0061] Step 404 may result in the formation of a metal layer comprising platinum metal and particles of a supplementary constituent, e.g., chromium particles, embedded or entrapped within the platinum metal (see, e.g., Figures

6A-B, 7A-B).

[0062] Step 406 may be similar to step 308 as described hereinabove with reference to method 300 (Figure 2). In some embodiments, step 406 may involve performing a first heat treatment, or annealing, the substrate. The first heat treatment may be performed at a relatively low temperature sufficient to promote bonding of the electrodeposited layer to the substrate surface. A temperature in the range of from about 550 to 650° C may be sufficient to promote such bonding of the electrodeposited layer to the substrate surface.

[0063] Alternatively, the first heat treatment may be performed at a relatively high temperature sufficient to promote interdiffusion of constituents of the electrodeposited layer with the adjacent surface layer of the substrate surface. A temperature in the range of from about 1000 to 1100° C may be sufficient to promote such diffusion of constituents of the electrodeposited layer and the substrate. When a heat treatment in the 1000 to 1100° C range is performed, the resulting coating may comprise a solid solution alloy; e.g., the coating may comprise a metallic solid solution of Ni, Pt and Cr when the substrate is a nickel-base alloy. Step 406 may be performed, for a period in the range of from about 15 minutes to four (4) hours, in a protective atmosphere (e.g., in argon), or under vacuum. In some embodiments, step 406 may be omitted.

[0064] Step 408 may involve depositing aluminum on the substrate or electrodeposited layer. The aluminum may be deposited on the substrate using various techniques known in the art, such as chemical vapor deposition (CVD), above the pack, pack aluminizing, physical vapor deposition, or as an aluminum powder slurry. Depending on the deposition technique, step 408 may typically be performed at a temperature in the range of from room temperature to 1100° C. Aluminizing processes conducted above about 800°C may promote interdiffusion of coating elements with the surface layer of the substrate.

[0065] Step 410 may involve performing a second heat treatment on the substrate to form a coating on the substrate. The coating may comprise a

platinum aluminide and one or more supplementary constituents. The supplementary constituent(s) may comprise chromium or chromium oxide. The supplementary constituent(s) may alternatively comprise one or more reactive elements, such Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In some embodiments, the supplementary constituent(s) may comprise chromium or chromium oxide, and may further comprise one or more of the reactive elements, such Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In other embodiments, the supplementary metal element(s) may comprise a chromium alloy comprising one or more metals such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Step 410 may be performed in a protective atmosphere (e.g., in argon), or under vacuum.

[0066] The coating formed according to method 400 may have those characteristics, features and elements as described hereinabove, for example, with reference to Figures 1A-B. Thus, the coating formed according to method 400 may serve as a corrosion resistant coating. The coating may also serve as an oxidation resistant coating.

[0067] Step 410 may be performed at a relatively high temperature sufficient to promote interdiffusion of constituents of the electrodeposited layer, the aluminum-rich layer, and the surface layer of the substrate. For example, the second heat treatment may be performed at a temperature sufficient to promote diffusion of aluminum with the electrodeposited platinum and chromium, and nickel from the surface layer of a superalloy substrate. Step 410 may be performed at a temperature in the range of from about 1000 to 1100° C, and for a period in the range of from about 15 minutes to four (4) hours. The resulting heat-treated coating may typically comprise a high melting temperature matrix phase, such as (Pt, Ni) Al intermetallic phase, which has finite solubility for the supplementary constituents. Chromium solubility within the (Pt, Ni) Al matrix phase may be limited to a few percent. Excess chromium may be present as discrete particles within the coating.

[0068] In contrast to certain line-of-sight deposition and coating

techniques of the prior art, methods and processes of the instant invention, for example method 400, can be used to form a uniform coating on substrates having complex geometry.

[0069] Figure 4 schematically represents a series of steps involved in a method 500 for coating a component, according to another embodiment of the invention. Step 502 may involve providing a substrate, for example, generally as described hereinabove with respect to step 302, method 300. Step 504 may involve forming a bond coating on the substrate. The bond coating formed in step 504 may be a platinum aluminide coating comprising platinum metal and chromium or a supplementary constituent that enhances oxide scale adhesion, such as Y, Zr, Hf, La, or Sc. The bond coating formed in step 504 may be formed generally as described hereinabove for steps 404 through 410 of method 400 (Figure 3).

[0070] Step 506 may involve forming an additional layer on the bond coating. In some embodiments, the additional layer formed in step 506 may be a thermal barrier coating. As an example, a thermal barrier coating formed on the bond coating may comprise a stabilized zirconia, such as an yttria stabilized zirconia. A thermal barrier coating formed on the bond coating may be deposited by various deposition processes known in the art, such as electron beam physical vapor deposition (EB-PVD) or a plasma spray process. A thermal barrier coating is disclosed in commonly assigned, co-pending U.S. Patent Application Serial No. 10/621,981, filed July 16, 2003 (entitled: *Thermal Barrier Coating with Stabilized Compliant Microstructure*), the disclosure of which is incorporated by reference herein in its entirety.

[0071] Figures 5A-D schematically represent stages in preparing a corrosion- and/or oxidation protective coating, according to one embodiment of the instant invention. Figure 5A represents a substrate 202 as seen in cross-section. Figure 5B represents substrate 202 having an electrodeposited layer 204 disposed thereon. Electrodeposited layer 204 may comprise electrodeposited platinum metal, together with entrapped particles of a

supplementary constituent. The supplementary constituent may comprise particles of chromium or chromium oxide. The supplementary constituent may further comprise particles of a reactive element such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In some embodiments, the supplementary constituent may comprise particles of an alloy comprising chromium and one or more of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. According to one aspect of the invention, electrodeposited layer 204 may be deposited in a single electrolytic step via an electrolyte composition comprising a platinum salt and particles of a suspended supplementary constituent.

[0072] Figure 5C represents an aluminized substrate 202 having an aluminum layer 206 deposited on electrodeposited layer 204. Figure 5D represents a platinum aluminide coating 210 on substrate 202. Platinum aluminide coating 210 may be formed from electrodeposited layer 204, and aluminum layer 206, and the surface layer of the substrate following heat treatment. The heat treatment may be sufficient to interdiffuse at least a portion of electrodeposited layer 204 and aluminum layer 206 with the surface layer of substrate 202. The heat treatment may also be sufficient to dissolve entrapped particles of a supplementary constituent (e.g., chromium), permitting it to become a constituent in the intermetallic solid solution matrix phase of the platinum aluminide coating.

EXAMPLES

Example 1

[0073] A solution comprising 12 g/L Pt and 100 g/L Na_2CO_3 was prepared by dissolving 40 g dinitrodiamine platinum ($Pt(NH_3)_2NO_2)_2$) (60.0 % Pt), and 200 g Na_2CO_3, in 2 L water. Electrolyte compositions were prepared from the solution by adding various amounts of Cr metal powder (Reade Advanced Materials, Providence, Rhode Island USA) to the dinitrodiamine

Pt/Na_2CO_3 solution. The Cr metal powder had a particle size of about 4 microns.

[0074] A nickel (Ni) sheet 2.54 cm x 1.27 cm x 0.080 cm (6.5 cm^2) was mechanically polished and chemically activated in 18% HCl for 1 min (per ASTM B558-79, 4.6). The Ni sheet was electroplated for 1 h using 2 Pt anodes at a voltage of 1.80 V, current density 2.0-2.9 A/dm^2, at a bath temperature of 82 to 86° C with magnetic stirring of the electrolyte.

Example 2

[0075] A Cr containing Pt metal layer (Pt + Cr layer) was electrodeposited on a Ni sheet from a Pt electrolyte composition (prepared according to Example 1) containing 10 g/L Cr metal powder. The weight of the Ni sheet prior to plating was 2.161 g. The weight of the Ni sheet with the Pt + Cr electroplated layer was 2.282 g. The weight of the Pt + Cr electroplated layer was 0.121 g. The thickness of the Pt + Cr electroplated layer was calculated from weight gain to be 8.7 microns, assuming that the electroplated layer consists of pure Pt.

Example 3

[0076] A Ni sheet electroplated with a Cr containing platinum (Pt + Cr) layer was annealed at 600° C for 30 min in argon. A scanning electron micrograph (original magnification, 2,500X) of a polished section of the Pt + Cr electroplated layer 204 is shown in Figure 6A. Cr particles, entrapped within the volume of the Pt metal of the electroplated layer, are clearly visible. No gaps are visible around the Cr particles. Similarly, there appears to be good bonding between the Pt and Ni substrate. The thickness of the Pt + Cr electroplated layer is mostly less than about 10 microns. Figure 6B is an energy-dispersive x-ray (EDX) spectrum taken from the image area of Figure 6A, indicating elemental x-ray peaks for Pt, Cr, and Ni.

[0077] Figure 7A is a higher magnification scanning electron micrograph (original magnification, 20,000X) of a polished section of the Pt + Cr electroplated layer. Figure 7A clearly shows a Cr particle entrapped within the Pt metal of the electroplated layer. Figure 7B is an energy-dispersive x-ray (EDX) spectrum taken from the Cr particle shown in Figure 7A. Figure 7B indicates elemental x-ray peaks for Cr and Pt.

Example 4

[0078] A Ni sheet electroplated with a Cr containing platinum (Pt + Cr) layer as described hereinabove was heat treated at 1065° C for 60 min in argon. A scanning electron micrograph (original magnification, 1,500X) of the Pt + Cr electroplated layer after heat treatment is shown in Figure 8A. Cr particles are no longer visible, indicating that heat treatment at 1065° C for 60 min may be sufficient to diffuse or dissolve the Cr, as well as the surface of the nickel substrate, into the platinum metal.

[0079] Figure 8B is an energy-dispersive x-ray (EDX) line-scan corresponding to the profile of the image area of Figure 8A. Figure 8B shows the elemental x-ray profile for Pt, Cr, and Ni from the surface of the electroplated and annealed layer to the Ni substrate. It can be seen that, in the region of the electroplated layer/substrate interface, the Pt concentration decreases and the Ni concentration increases with increasing distance from the surface. The concentration of Cr remains approximately constant until the Pt level begins to decline.

[0080] It should be understood, of course, that the foregoing relates to preferred embodiments of the invention and that modifications may be made without departing from the spirit and scope of the invention as set forth in the following claims.

WE CLAIM:

1. A method for electroplating platinum, comprising:

a) providing a substrate; and

b) electrolytically depositing a metal layer on a surface of said substrate, wherein said metal layer comprises platinum and a supplementary constituent,

wherein said metal layer is deposited from a single electrolyte composition during a single electrolytic step,

wherein said electrolyte composition comprises a platinum salt and particles of said supplementary constituent, and

wherein said particles of said supplementary constituent are deposited in said metal layer from said electrolyte composition.

2. The method of claim 1, wherein said supplementary constituent comprises at least one element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

3. The method of claim 1, wherein said supplementary constituent comprises chromium oxide or chromium.

4. The method of claim 1, wherein said supplementary constituent comprises chromium oxide, and at least one reactive element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

5. The method of claim 1, wherein said supplementary constituent comprises a chromium alloy including at least one metal selected from the group consisting of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

6. The method of claim 1, wherein said particles of said supplementary constituent have a mean diameter of from about 1 to 50 microns.

7. The method of claim 1, wherein said particles of said supplementary constituent comprise a mixture of chromium powder and particles of at least one reactive element selected from the group consisting of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

8. The method of claim 1, wherein said substrate comprises an alloy, and the method further comprises:

c) after said step b), aluminizing said substrate; and

d) heating said substrate to form an intermetallic matrix coating, wherein said intermetallic matrix coating comprises platinum, aluminum, said supplementary constituent, and constituents of said alloy substrate.

9. The method of claim 1, wherein said electrolytically deposited metal layer forms a coating on a surface of said substrate, said coating comprising said supplementary constituent, and said substrate comprising an alloy, and the method further comprising:

after said step b), heat treating said coating and said substrate surface to form a metallic solid solution comprising platinum metal, said supplementary constituent, and constituents of said substrate.

10. A method for electroplating platinum on a substrate, comprising:

a) electroplating platinum metal on said substrate via an electrolyte comprising particles of a supplementary constituent; and

b) concurrently with said step a), depositing said particles of said supplementary constituent on said substrate,

wherein said supplementary constituent is selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

11. The method of claim 10, wherein said particles of said supplementary constituent are entrapped within said platinum metal.

12. The method of claim 10, wherein said particles of said supplementary constituent comprise chromium metal powder.

13. The method of claim 10, wherein said electrolyte comprises dinitrodiamine platinum.

14. The method of claim 10, wherein said step a) comprises applying a voltage of from about 1.2 to 2.2 volts between said substrate and an anode.

15. A process for preparing a coated component, comprising:

a) providing a substrate;

b) electroplating a metal layer on a surface of said substrate, wherein said electroplated metal layer comprises platinum metal and particles of at least one supplementary constituent entrapped within said platinum metal, wherein said at least one supplementary constituent is selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re;

c) depositing aluminum on said electroplated metal layer; and

d) forming a platinum aluminide coating on said substrate, wherein said platinum aluminide coating comprises said at least one supplementary constituent.

16. The process of claim 15, wherein said particles and said platinum metal are co-deposited from a single electrolyte composition, and said electrolyte composition comprising said particles.

17. The process of claim 16, further comprising:

e) during said step b), maintaining said particles in suspension.

18. The process of claim 16, wherein said electrolyte composition comprises from about 0.2 to 400 g/L of said particles, and wherein said particles comprise chromium metal powder.

19. The process of claim 15, further comprising:

f) after said step b) and prior to said step c), heating said substrate.

20. The process of claim 19, wherein said step f) comprises heating said substrate to a temperature sufficient to bond said electroplated metal layer to said substrate.

21. The process of claim 20, wherein said temperature sufficient to bond said electroplated metal layer to said substrate is in the range of from about 300 to 650° C.

22. The process of claim 19, wherein said step f) comprises heating said substrate to a temperature sufficient to interdiffuse at least a portion of said electroplated metal layer with said substrate.

23. The process of claim 22, wherein said temperature sufficient to interdiffuse at least a portion of said electroplated metal layer with said substrate is in the range of from about 1000 to 1100° C.

24. The process of claim 15, wherein said substrate comprises an alloy, and wherein said step d) comprises heating said substrate to a temperature sufficient to form said platinum-aluminide coating from said platinum metal, said particles of said at least one supplementary constituent, and constituents of said substrate, wherein said platinum-aluminide coating comprises an intermetallic or metallic solid solution phase, wherein said intermetallic or metallic solid solution phase comprises Pt, Al, said at least one supplementary constituent, and said constituents of said substrate.

25. The process of claim 15, wherein said step d) comprises heating said substrate to a temperature in the range of from about 1000 to 1100° C.

26. A coating for a substrate, said coating prepared according to the process of claim 11.

27. A process for preparing a coated component, comprising:

a) providing a substrate;

b) electroplating a platinum metal layer on said substrate, wherein said platinum metal layer is electrodeposited via an electrolyte composition comprising chromium particles;

c) concurrently with said step b), depositing said chromium particles on said substrate, wherein said chromium particles are entrapped within said platinum metal layer;

d) optionally, exposing said substrate to a first heat treatment;

e) thereafter, aluminizing said substrate; and

f) exposing said substrate to a second heat treatment to form a platinum aluminide coating on said substrate, wherein said platinum aluminide coating comprises:

chromium within an intermetallic solid solution phase, and

said chromium particles dispersed within said intermetallic solid solution phase.

28. The process of claim 27, wherein said electrolyte composition further comprises dinitrodiamine platinum.

29. The process of claim 27, wherein said electrolyte composition further comprises at least one reactive element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

30. The process of claim 27, further comprising:

g) during said step b), stirring said electrolyte composition to maintain said chromium particles in suspension.

31. A component comprising:

a metal substrate; and

a platinum aluminide coating disposed on said substrate, wherein said platinum aluminide coating comprises platinum and a supplementary constituent comprising at least one element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re,

wherein said supplementary constituent is co-electrodeposited with said platinum,

wherein during a heat treatment said supplementary constituent at least partially dissolves and is incorporated into an intermetallic phase or at least one solid solution phase,

wherein said intermetallic phase or said at least one solid solution phase is formed by reaction of said platinum, said aluminum, and constituents of said metal substrate, and

wherein said coating is substantially free from chlorine, sulfur, phosphorus, or compounds thereof.

32. The component of claim 31, wherein:

said platinum aluminide coating comprises a bond coating, and

said component further comprises a thermal barrier coating disposed on said bond coating.

33. The component of claim 32, wherein said thermal barrier coating comprises a stabilized zirconia.

34. The component of claim 31, wherein said substrate comprises iron-, nickel-, or cobalt-base alloys or a nickel-base superalloy.

35. The component of claim 31, wherein said substrate comprises a blade or vane for a gas turbine engine.

36. A corrosion and oxidation resistant coating, comprising:

electrodeposited platinum;

a supplementary constituent, wherein said supplementary constituent is co-electrodeposited with said platinum; and

deposited aluminum;

wherein said corrosion- and oxidation resistant coating comprises a platinum aluminide coating, said platinum aluminide coating consisting primarily of at least one intermetallic solid solution phase, and

wherein said supplementary constituent is chromium, and wherein said coating is substantially free from chlorine, sulfur, phosphorus, or compounds thereof.

37. The coating of claim 36, wherein said coating has a thickness in the range of from about 5 to 100 microns.

38. The coating of claim 36, wherein said coating comprises from about 2 to 35 weight % chromium.

39. The coating of claim 36, wherein said coating comprises from about 15 to 25 weight % chromium, and from about 10 to 30 weight % aluminum.

40. An electrolyte composition for electrodeposition of platinum, comprising:

a platinum salt;

a carbonate or bicarbonate of an alkali metal; and

particles of at least one supplementary constituent, wherein said at least one supplementary constituent is selected from the group consisting of chromium, chromium oxide, a chromium alloy, and a reactive element, and wherein said reactive element is selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

41. The electrolyte of claim 40, wherein said platinum salt comprises dinitrodiamine platinum, and wherein said electrolyte is substantially free from chlorine, sulfur, phosphorus, or compounds thereof.

42. The electrolyte of claim 40, wherein said at least one supplementary constituent comprises from about 0.1 to 80 g/L, and wherein said particles have a mean diameter in the range of from about 1 to 50 microns.

43. An electrolyte composition for electrodeposition of platinum, comprising:

dinitrodiamine platinum;

an alkali metal carbonate or bicarbonate; and

chromium metal powder in an amount of from about 0.2 to 80 g/L.

44. The electrolyte of claim 43, wherein said dinitrodiamine platinum comprises from about 25 to 55 g/L.

45. The electrolyte of claim 43, wherein said alkali metal carbonate or bicarbonate comprises from about 1 to 200 g/L.

46. The electrolyte of claim 43, wherein said chromium metal powder comprises chromium particles having a mean diameter in the range of from about 1 to 50 microns.

47. The electrolyte of claim 43, further comprising particles of at least one reactive element selected from the group consisting of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

48. The electrolyte of claim 47, wherein said reactive element is selected from the group consisting of Y, Zr, Hf, La, and Sc.

PLATINUM ALUMINIDE COATING & METHOD THEREOF

ABSTRACT OF THE DISCLOSURE

Platinum containing coatings for corrosion and oxidation protection of a substrate, and platinum electrodeposition methods for coating a substrate. The coating may comprise platinum and at least one supplementary constituent, and the method may involve co-electrodeposition of platinum and the supplementary constituent from a single electrolyte composition. The supplementary constituent may comprise chromium, an oxidation protective reactive element, or an alloy of chromium with a reactive element. Components protected by such coatings are also disclosed.

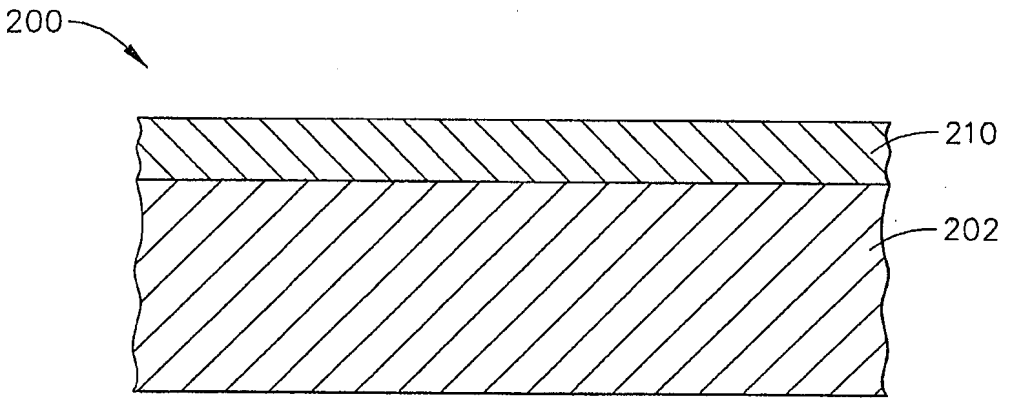

FIG. 1A

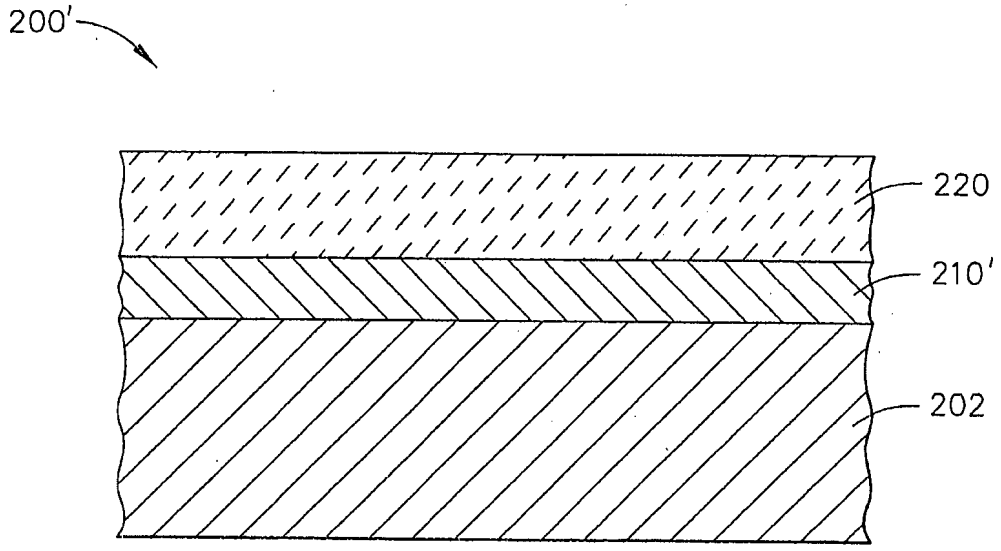

FIG. 1B

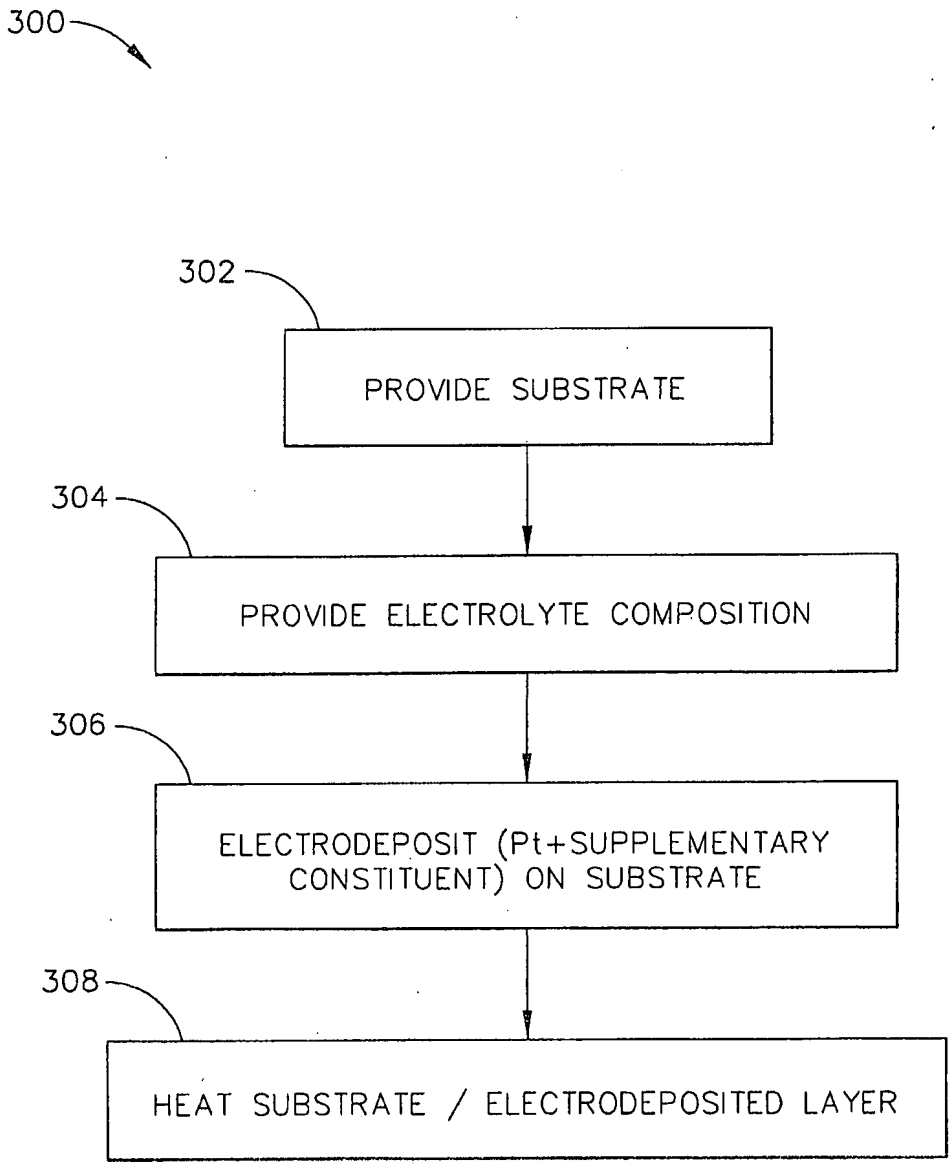
300
302
PROVIDE SUBSTRATE
304
PROVIDE ELECTROLYTE COMPOSITION
306
ELECTRODEPOSIT (Pt+SUPPLEMENTARY CONSTITUENT) ON SUBSTRATE
308
HEAT SUBSTRATE / ELECTRODEPOSITED LAYER

FIG. 2

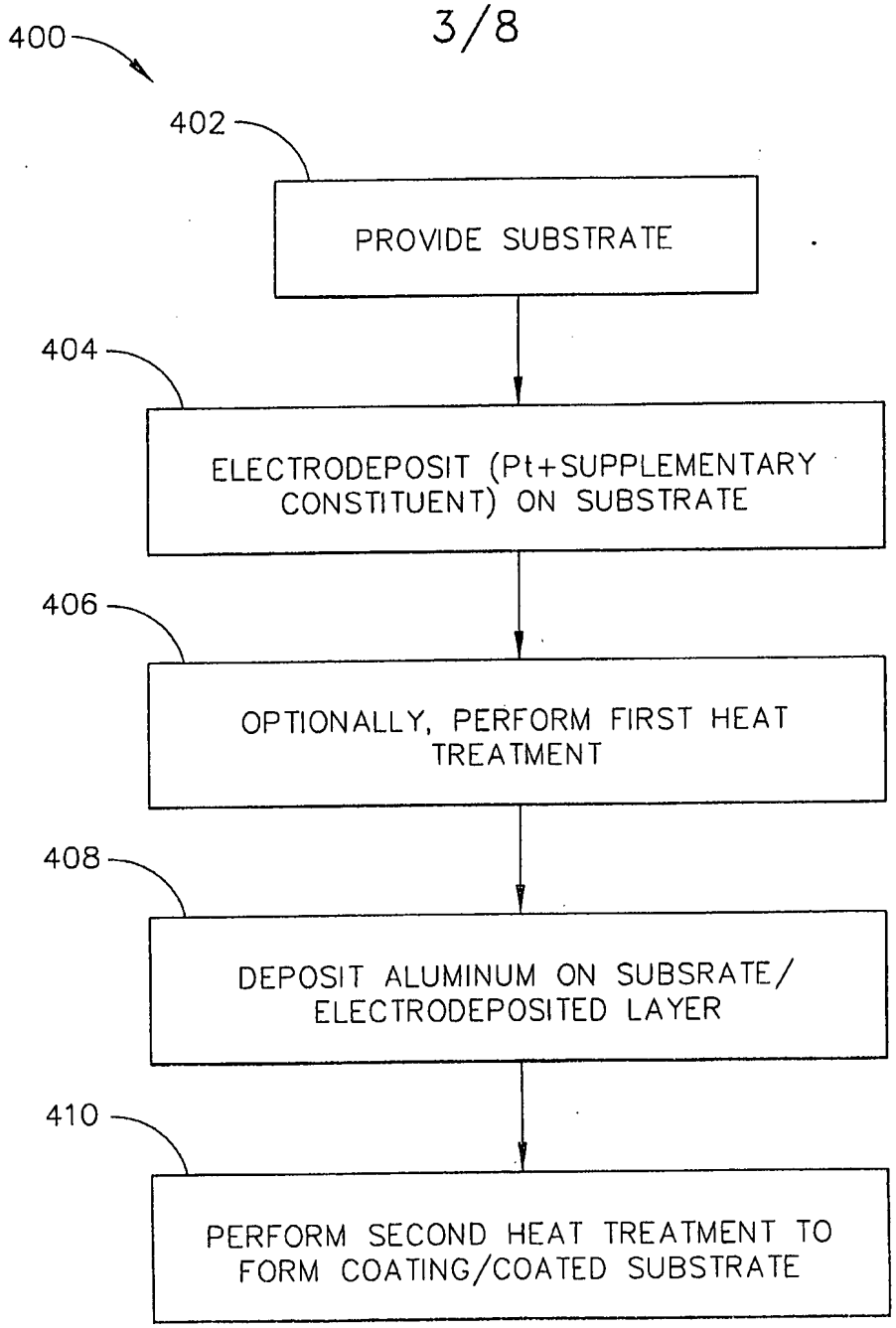
400
402
PROVIDE SUBSTRATE
404
ELECTRODEPOSIT (Pt+SUPPLEMENTARY CONSTITUENT) ON SUBSTRATE
406
OPTIONALLY, PERFORM FIRST HEAT TREATMENT
408
DEPOSIT ALUMINUM ON SUBSRATE/ ELECTRODEPOSITED LAYER
410
PERFORM SECOND HEAT TREATMENT TO FORM COATING/COATED SUBSTRATE

FIG. 3

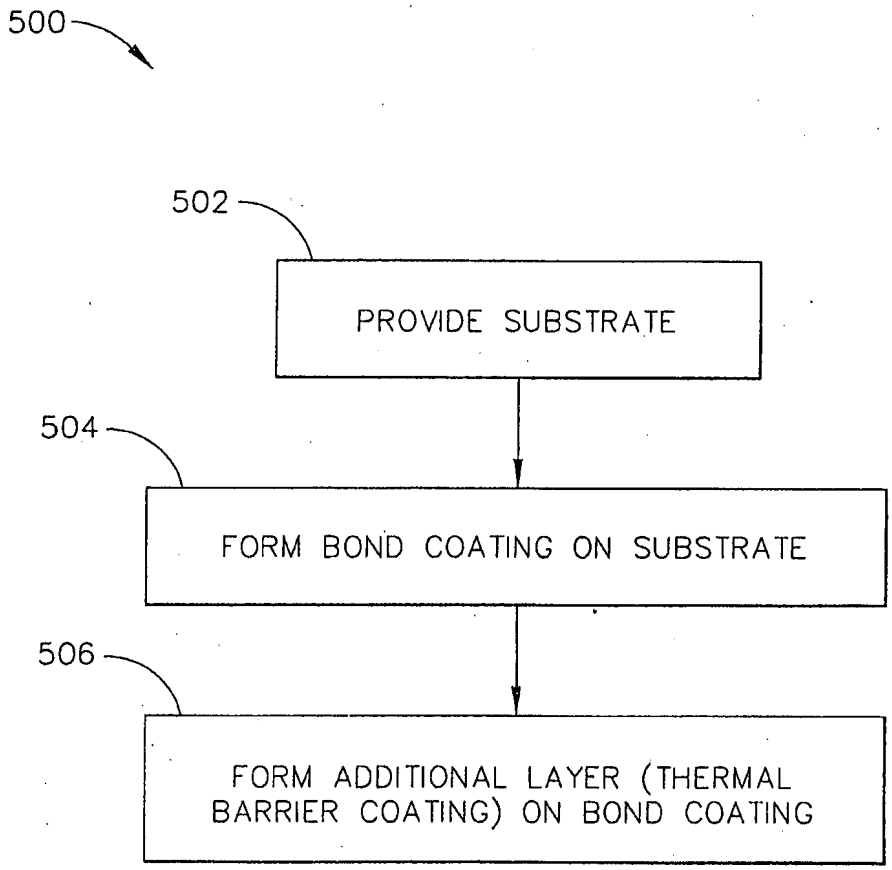
500
502
PROVIDE SUBSTRATE
504
FORM BOND COATING ON SUBSTRATE
506
FORM ADDITIONAL LAYER (THERMAL BARRIER COATING) ON BOND COATING

FIG. 4

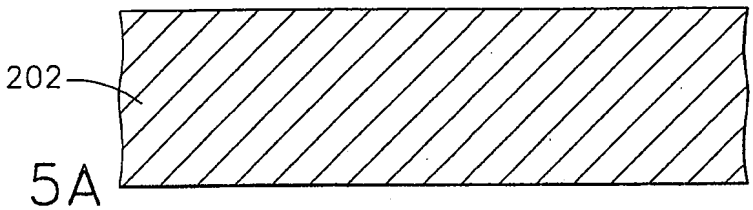

FIG. 5A

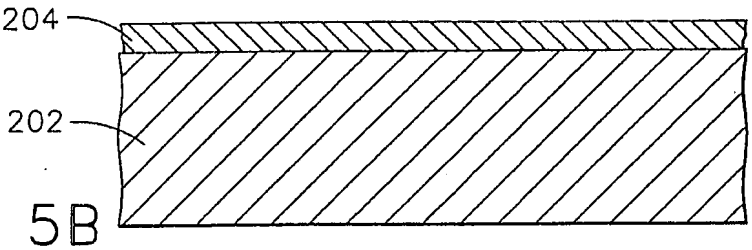

FIG. 5B

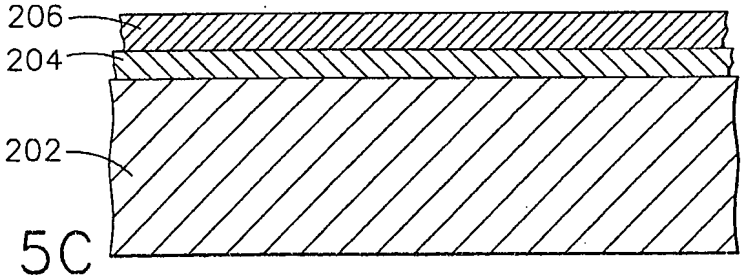

FIG. 5C

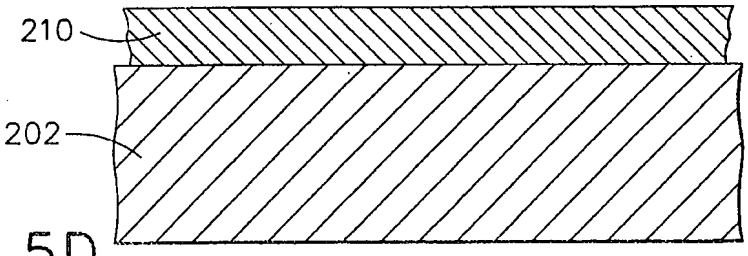

FIG. 5D

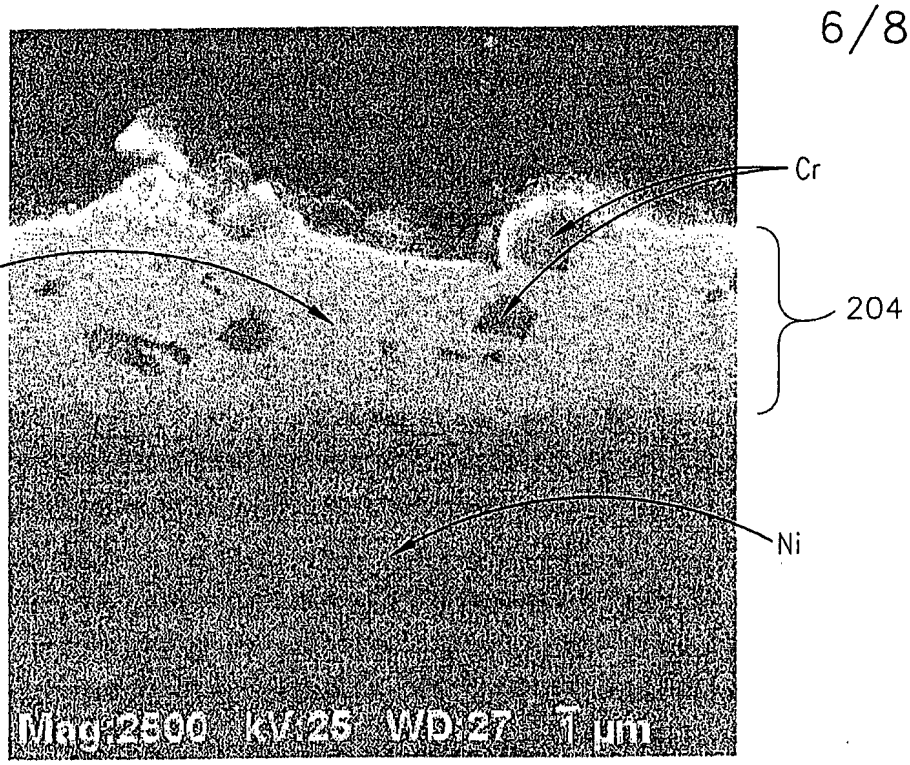
Cr
Pt
204
Ni
Mag=2800 kV=25 WD=27 1 um

FIG. 6A

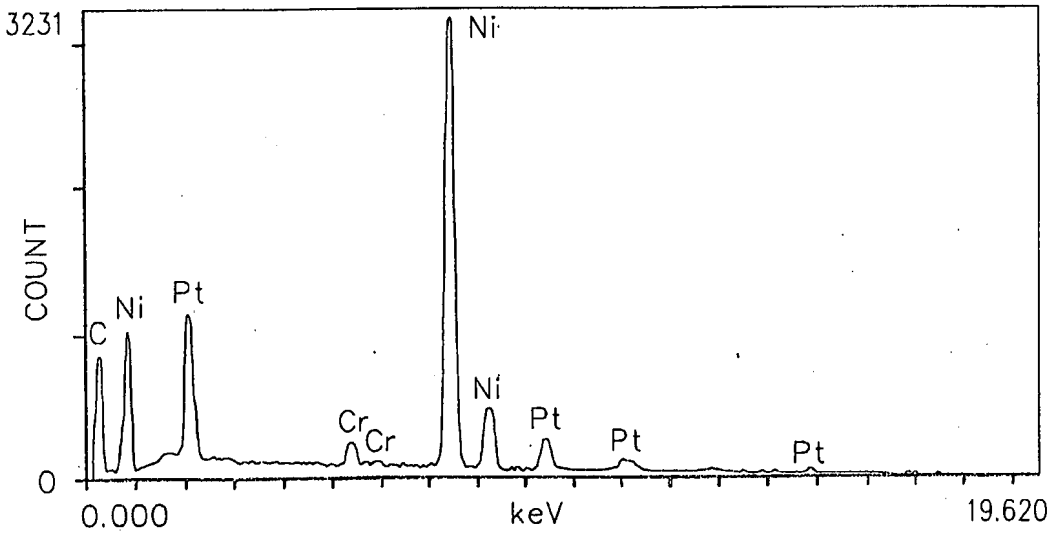
3231
Ni
COUNT
C
Ni
Pt
Cr
Cr
Ni
Pt
Pt
Pt
0
0.000
keV
19.620

FIG. 6B

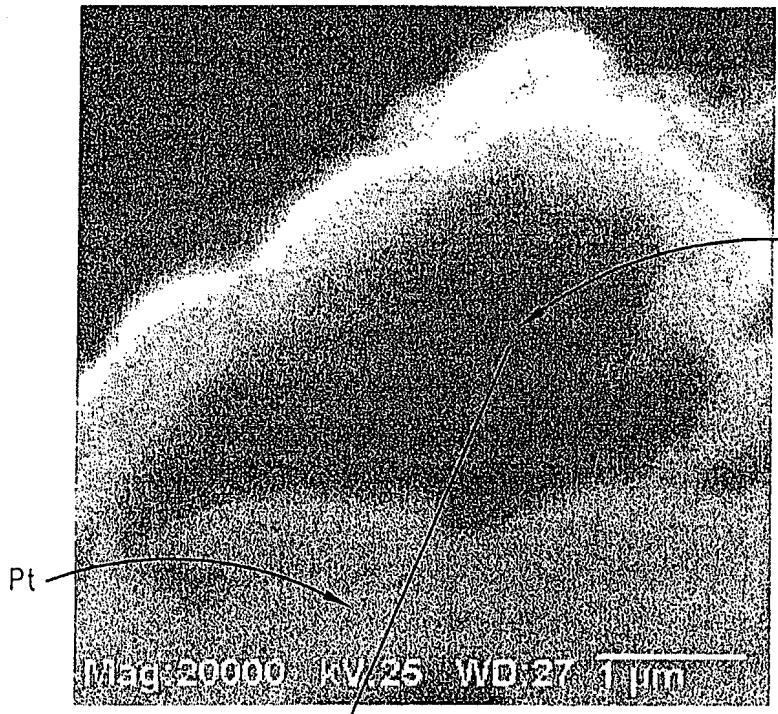
Cr
Pt
Mag 20000 kV 25 WD 27 1 µm

FIG. 7A

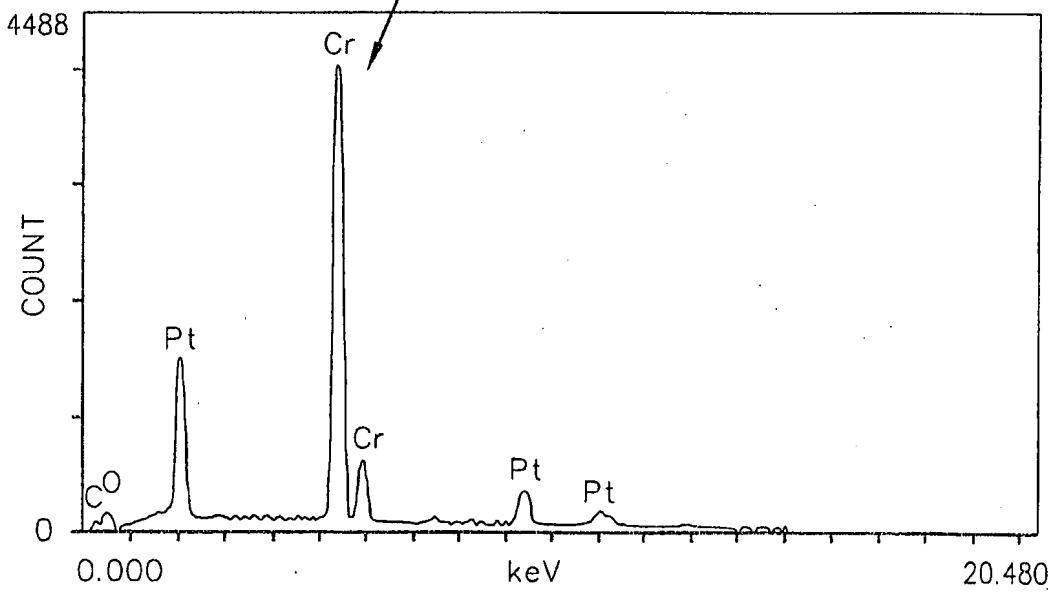
4488
Cr
COUNT
Pt
Cr
C
O
Pt
Pt
0
0.000
keV
20.480

FIG. 7B

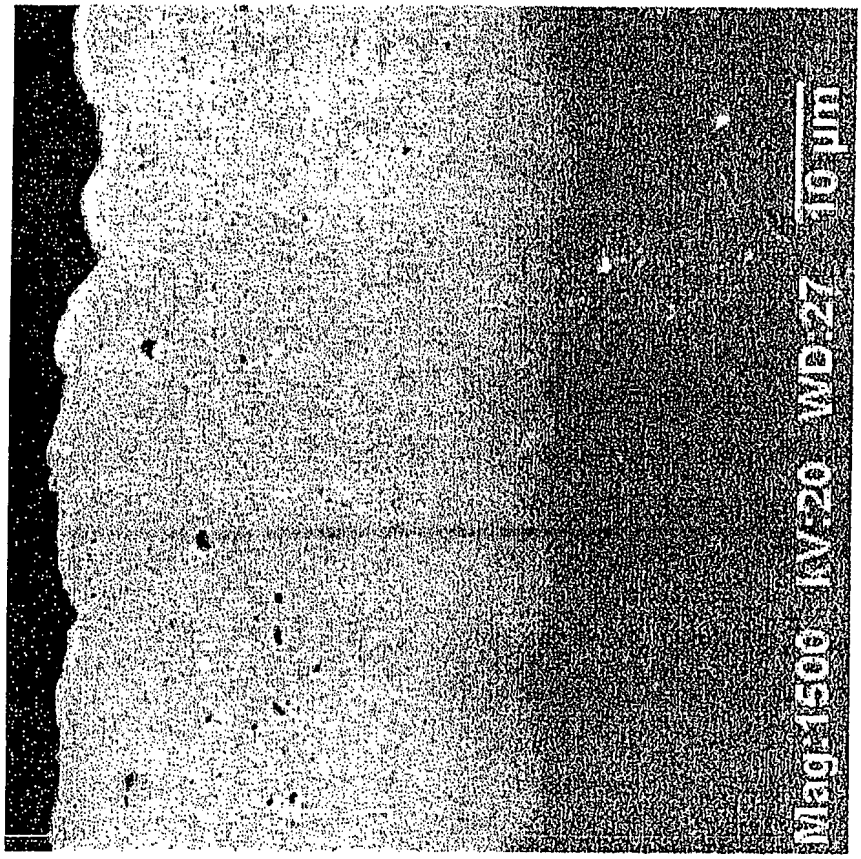

FIG. 8A

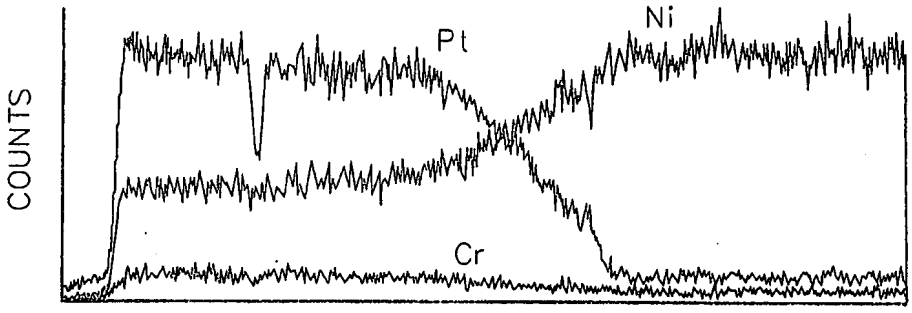

FIG. 8B

Page 1 of 2

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Cindy Kwacala
Ingrassia, Fisher & Lorenz
7010 E. Cochise Road

Scottsdale, AZ 85253

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Ship Date: 03SEP08
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TO EXPOSE ADHESIVE REMOVE LINER

Fold or Peel along Bottom of Peel and Stick Airbill or Pouch

Missy Hale

From: TrackingUpdates@fedex.com
Sent: Wednesday, September 17, 2008 6:36 AM
To: Missy Hale
Subject: FedEx Delivery Exception

This tracking update has been requested by:

Company Name:	INGRASSIA FISHER & LORENZ, P.C
Name:	Cindy Kwacala
E-mail:	'not provided by requestor'

FedEx attempted, but was unable to complete delivery of the following shipment:

Reference:	002.3315
Ship (P/U) date:	Sep 3, 2008
Estimated delivery:	Sep 12, 2008
Service type:	FedEx International Economy
Packaging type:	FedEx Envelope
Number of pieces:	1
Weight:	0.70 lb.
Special handling/Services	Deliver Weekday

Tracking number: 799899076842

Reason Delivery Not Completed	Recommended Action
1. Unable to deliver shipment, returned to shipper	No action is required. The package is being returned to the shipper.

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UTILITY PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Alexander S. KOZLOV
Group Art Unit: 1753
Serial No.: 10/753,675
Examiner: H. D. Wilkins III
Filed: January 7, 2004
Confirmation No.: 1132
For: PLATINUM ALUMINIDE COATING AND METHOD THEREOF
Docket No.: H0005756

DECLARATION OF MISSY HALE

I, Missy Hale, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1000 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application and of any patent issuing therefrom.

1) I am a patent assistant for the law firm of Ingrassia, Fisher & Lorenz, 7010 East Cochise Road, Scottsdale, Arizona 85253 ("IF&L") which acts as outside counsel for client Honeywell International, Inc. of Law Dept. AB2, P.O. Box 2245, Morristown, New Jersey 07962-9806 ("Honeywell"). Part of my responsibility is to obtain signatures of Honeywell inventors on declarations in Honeywell patent applications.

2) I learned that Alexander S. Kozlov was deceased and that his sole surviving heir was Svetlana Kozlova, whose last known address was:

Golubinskaja 7, Korp 5 KV. 260
Moscow 117574, Russia

and, on September 6, 2008, I sent a package via Federal Express ("Federal Express package") that included a copy of the Combined Declaration and Power of Attorney, a copy of the Assignment, a letter in English to Ms. Kozlova requesting her signatures on the declaration and the assignment, a letter translated into Russian to Ms. Kozlova requesting her signatures on the declaration and the assignment, a copy of the specification, claims, and

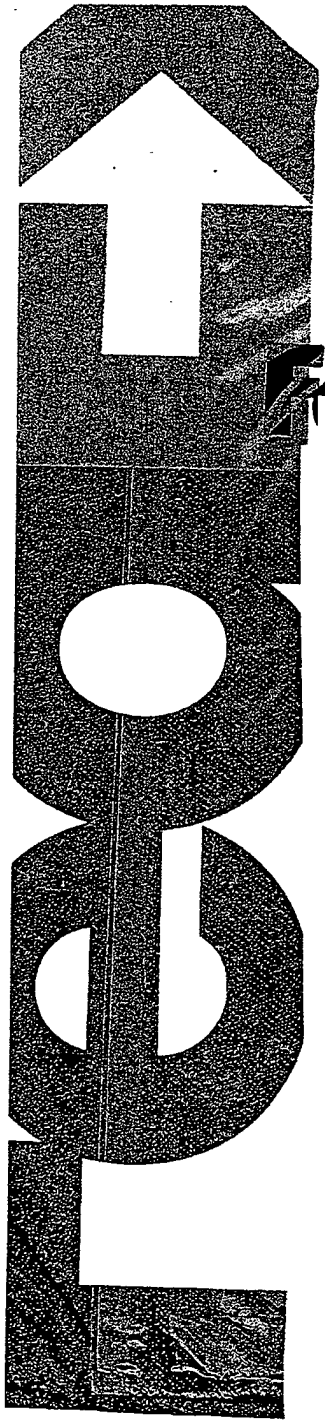
drawings of the above-referenced application, a self-addressed stamped Federal Express envelope to return the signed documents back to IF&L, and a listing of the package contents. A copy of the contents of the Federal Express package is attached.

3) On September 17, 2008, I received an email from Federal Express indicating that the Federal Express package had been undeliverable. A copy of the email is attached.

4) To date, IF&L has not received a returned signed copy of the Combined Declaration and Power of Attorney or the Assignment.

Date: October 14, 2008

Missy Hale



Page 2 of 2

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UNITED STATES

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Svetlana Kozlova

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Moscow, 117574
RU

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REF: 002.3315
DESC-1: Legal Documents
DESC-2:
DESC-3:
DESC-4:
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COUNTRY MFG: US
CARRIAGE VALUE: .00 USD
CUSTOMS VALUE: 100.00 USD
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PKG TYPE: ENV

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FedEx TRK# 0430 7998 9907 6842

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GOLUBINSKAJA 7, KORP 5 KV. 260,
MOSCOW, , RU, ** 117574 **

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MST

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ECON

INGRASSIA FISHER & LORENZ, P.C.

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JOANN M. SEATON
MARK M. TAKAHASHI •
JAMES R. WALTERS
• Admitted to practice in AZ

Patent Agent
David P. Mancini

VIA FEDERAL EXPRESSS

September 2, 2008

Svetlana Kozlova
Golubinskaja 7, Korp 5 KV. 260
Moscow 117574, Russia

Re: Alexander S. Kozlov
Our ref no.: H0005756

Dear Ms. Kozlova:

Our law firm represents Honeywell International Inc., the former employer of Alexander Kozlov. We understand that you are the daughter of Mr. Kozlov who resided in New Jersey, United States of America, and that you previously signed and returned documents relating to a patent on which he was an inventor.

To comply with a request from the United States Patent and Trademark Office, we need to obtain another signed version of the documents that you previously signed. Thus, I would greatly appreciate it if you would please re-sign the documents and send them to us by September 26, 2008. The documents are attached to this letter. If we do not receive the signed documents by September 26, we will need to file a Petition stating that we could not reach you.

Because the deadline is approaching, please fax the signed documents to us at (480) 385 0 61, and please return the original version using the mail system. For your convenience, we 've included a self-addressed, postage-prepaid envelope in which you may return the original 'sion of the signed documents.

Finally, please let me know if you would like a copy of your father's patent, and I will be glad to send it to you. Thank you for your assistance.

Very truly yours,

INGRASSIA FISHER & LORENZ, P.C.

Cindy H. Kwacala

Cindy H. Kwacala

List of documents included in envelope

Letter (English version)
Copy of letter (Russian version)
Declaration
Assignment
Patent Application and drawings
Self-Address Pre-paid Return Federal Express Envelope

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MARK M. TAKAHASHI •
JAMES R. WALTERS
• Admitted to practice in AZ

Patent Agent
David P. Mancini

ЗАКАЗНОЙ ПОЧТОЙ
С ПОДПИСЬЮ АДРЕСАТА О ПОЛУЧЕНИИ

2 сентября 2008г.

Россия, Москва- 117574,
ул. Голубинская, 7, корп. 5, кв. 260,
г-же Светлане Козловой

Кас.: Александр С. Козлов
Наш спр. №: H0005756

Уважаемая г-жа Козлова!

Наша юридическая фирма представляет компанию Honeywell International Inc., где в прошлом работал Александр Козлов. Насколько нам известно, Вы являетесь дочерью г-на Козлова, который проживал в Нью Джерси, Соединенные Штаты Америки, и в прошлом Вы подписали и вернули документы, связанные с патентом, изобретателем которого он является.

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Сообщите мне, пожалуйста, нужна ли Вам копия патента Вашего отца, я буду рада отправить ее Вам. Благодарю Вас за помощь.

С уважением,

INGRASSIA FISHER & LORENZ, P.C.

Синди Х. Ювакала

United States Patent Application
Attorney Docket No.: H0005756
First Named Inventor: Alexander S. Kozlov

DECLARATION FOR A UNITED STATES PATENT APPLICATION
(Equivalent to PTO/SB/01)

As a below named inventor, I hereby declare that:

My residence, mailing address, and country of citizenship are stated below next to my full name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter, which is claimed and for which a patent is sought on the invention entitled:

PLATINUM ALUMINIDE COATING AND METHOD THEREOF
the specification of which:
[ ] is attached hereto;
[X] was filed on January 7, 2004 and assigned U.S. application serial no. or PCT application no. 10/753,675;
[ ] and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment specifically referred to above, if any.

I hereby acknowledge the duty to disclose information which is material to patentability as defined by 37 C.F.R. § 1.56.

Authorization To Permit Access To Application by Participating Offices

[X] If checked, the undersigned hereby grants the USPTO authority, under 37 CFR 1.14(c) and (h), to provide the European Patent Office (EPO), the Japan Patent Office (JPO), and any other intellectual property offices in which a foreign application claiming priority to the above-identified application is filed access to the above-identified patent application.

Claim of Foreign Priority Benefits

I hereby claim foreign priority benefits under 35 U.S.C. 119 or 365 of any foreign application(s) for patent, inventor's or plant breeders rights certificate(s), listed below and have also identified below, any foreign application for patent, inventor's or plant breeders rights certificate(s), or of any PCT international application having a filing date before that of the application of which priority is claimed:

Foreign Application No.	Country	Foreign Filing Date

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States Provisional applications listed below:

Application No.	Filing Date

I hereby claim the benefit under 35 U.S.C. 120 or 365 of any United States application(s) or of any PCT international application designating the United States of America, listed below:

U.S. Parent Application or PCT Parent No.	Country	Foreign Filing Date

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I hereby declare that all statements made herein of my own knowledge are true and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signature of Sole or First Inventor: _____ Date:_____

Full Name of Sole or First Inventor: Alexander S. Kozlov, deceased and being represented by legal representative Svetlana Kozlova, whose signature appears above and whose Residence City, Residence Country, Citizenship, and Mailing Address are listed below

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Signature of Second Joint Inventor: _____ Date:_____

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Signature of Third Joint Inventor: _____ Date:_____

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City: Morristown State: NJ Zip Code: 07962-2245

United States Patent Application
Attorney Docket No.: H0005756
First Named Inventor: Alexander S. Kozlov

ASSIGNMENT

WHEREAS, the undersigned inventor(s) (hereinafter individually and collectively referred to as "ASSIGNOR") has/have invented:

PLATINUM ALUMINIDE COATING AND METHOD THEREOF

(hereinafter, "the invention") for which application for Letters Patent of the United States:

[ ] has been executed on even date herewith;

[ ] was executed on _____;

[X] was filed on January 7, 2004 and assigned U.S. application serial no. 10/753,675;

AND WHEREAS, Honeywell International Inc., a Delaware corporation having a place of business at 101 Columbia Road, POB 2245, Morristown, N.J. 07962-2245 (hereinafter "ASSIGNEE"), and its successors, assigns, and legal representatives, is desirous of acquiring, and the ASSIGNOR is desirous of assigning and transferring the entire right, title, and interest therein;

AND WHEREAS, a "formal application," as referred to herein, shall mean any provisional, nonprovisional, continuation, continuation in part, continued prosecution, substitute, renewal, extension, divisional, reissue, reexamination, foreign, Patent Cooperation Treaty (PCT) or other patent application, inventor's certificate, utility model, or like document;

NOW, THEREFORE, for good and valuable consideration, the receipt and sufficiency of which are hereby acknowledged, ASSIGNOR does hereby irrevocably and unconditionally assign and transfer unto ASSIGNEE, its successors, assigns, and legal representatives, the entire right, title and interest in and to the aforesaid application, to the invention as described in the aforesaid application, and to any formal application which may be filed based in whole or in part on the aforesaid application, in the United States and all foreign countries, together with the right of priority under any international conventions, treaties and/or agreements to which the United States currently adheres and adheres to in the future and with all ancillary rights thereto, including the right to sue and recover for, and the right to profits or damages due or accrued, arising our of or in connection with, any and all past, present or future infringements of any such rights, and hereby authorizes and requests the Commissioner of Patents to issue said Letters Patent to ASSIGNEE, for the sole use and benefit of ASSIGNEE, its successors, assigns, and legal representatives;

AND ASSIGNOR authorizes ASSIGNEE, its successors, assigns, and legal representatives, or anyone it may properly designate, to apply for Letters Patent, in its own name if desired, in any and all foreign countries, and additionally to claim the filing date of aforesaid application and/or otherwise take advantage of the provisions of any international convention, treaty and/or agreement;

AND ASSIGNOR FURTHERMORE authorizes ASSIGNEE, its successors, assigns, and legal representatives, or anyone it may properly designate, to insert in this instrument the filing date and/or serial number of said application when ascertained;

AND ASSIGNOR HEREBY AGREES to transfer, upon request of ASSIGNEE, its successors, assigns, and legal representatives, and without further remuneration, a like interest in and to any related inventions and formal applications based thereon;

AND ASSIGNOR AGREEING, FURTHERMORE, upon request of ASSIGNEE, and without further remuneration, but at no expense to ASSIGNOR, that ASSIGNOR will provide all reasonable assistance to obtain, maintain, and assert the fullest measure of legal protection that ASSIGNEE desires to obtain or assert for the invention, any related inventions, any formal application based thereon, and any resulting patents, including executing any and all papers desired by ASSIGNEE for the filing and granting of formal applications, the perfecting of title in ASSIGNEE, and in enforcing any rights in the invention, any related inventions, and any formal application or patent based thereon.

This instrument is executed by, an shall be binding upon, ASSIGNOR, his heirs, executors and administrators, for the uses and purposes above set forth and referred to and shall inure to the benefit of ASSIGNEE, its successors, assigns and legal representatives, or anyone it may properly designate.

If any provision of this assignment is held by any court to be unenforceable, such provision shall be interpreted to accomplish the objectives of the original provision to the fullest extent allowed by law and the remainder of this assignment shall remain in full force and effect.

EXECUTED as of the date(s) written below by ASSIGNOR:

_____ Date: _____

Alexander S. Kozlov, deceased and being represented by legal representative Svetlana Kozlova

_____ Date: _____

Derek Raybould

_____ Date: _____

Siu-Ching D. Lui

_____ Date: _____

Thomas E. Strangman

"Express Mail" label number EV374985827US

Date of deposit _____

I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to: MAIL STOP PATENT APPLICATION, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Michael A. Shimokaji, Reg. No. 32,303

PATENT
H0005756-1060

PLATINUM ALUMINIDE COATING AND METHOD THEREOF

BACKGROUND OF THE INVENTION

[0001] The present invention generally relates to co-electrodeposition of platinum and a supplementary constituent to platinum aluminide coatings, and to methods for forming such coatings.

[0002] In modern gas turbine engines, the blades and vanes in the high pressure turbine section are exposed to temperatures in excess of 1000° C for extended periods of time. Superalloy gas turbine engine components are commonly coated with platinum aluminide coatings to inhibit oxidation and corrosion of the superalloy surface. Protection provided by platinum aluminide coatings is due to selective oxidation of aluminum to form an alumina (Al_2O_3) scale that grows very slowly at high temperature by a diffusion process.

[0003] Impurities within the platinum aluminide coating, e.g., sulfur (S), phosphorus (P), and chlorine (Cl), can segregate to the interface between the coating and the alumina scale, weaken the interface, and thus promote spalling of the protective oxide scale. Periodic oxide spalling accelerates the consumption of aluminum from the platinum aluminide coating and reduces the oxidation life of the component. Impurity-induced oxide spalling of the protective oxide scale also limits the life of thermal barrier coatings that utilize platinum aluminide coatings as a bond coating.

[0004] U.S. Patent No. 6,306,277 to Strangman *et al.* discloses an electroplating process for electrodeposition of platinum on superalloy substrates, and a platinum electrolyte for use in such electroplating process, wherein the electrolyte is stable and readily prepared. The electrolyte

comprises the platinum salt, dinitrodiamine platinum ($Pt(NH_3)_2(NO_2)_2$), and an alkali metal carbonate or bicarbonate; and the process results in decreased contaminant levels of S, Cl, and P in the electroplated Pt layer, as compared with Pt layers deposited using prior art electrolytes.

[0005] It is known that the presence of chromium (Cr) in superalloy coatings (e.g., Cr containing platinum aluminide coatings) increases the corrosion resistance of superalloy components, and hence increases the life of such components, as compared with platinum aluminide coatings which substantially lack Cr.

[0006] EP 0821076 A1 to Wing discloses a process for forming a platinum aluminized chromised Ni-based superalloy, wherein the process involves the steps of: 1. forming a chromium enriched surface layer of the superalloy, e.g., by electroplating; 2. heating in a vacuum or protective atmosphere; 3. forming a platinum layer on the chromium enriched superalloy by electroplating, sputtering, etc.; 4. heating in a vacuum or protective atmosphere for one to four hours at 900° to 1150° C; and 5. aluminizing the chromised, diffused, platinum coated Ni-based superalloy, e.g., by out of pack aluminizing for six hours at 1080° C. Thus, in the process of Wing, Cr and Pt are deposited on the superalloy in separate steps.

[0007] U.S. Patent No. 5,482,578 to Rose *et al.* discloses a diffusion coating process for the deposition of a coating of chromium-containing $PtAl_2$ on a superalloy substrate. The process of the '578 patent involves: 1. deposition of a platinum group metal on the superalloy, e.g., by electroplating; 2. heating *in vacuo* at about 1900° F for about an hour; 3. diffusion coating the platinum-group metallized superalloy with an Al/Cr powder; and finally 4. heat treating the Al/Cr diffusion coated, metallized superalloy at about 1925° to 2050° F in hydrogen for about one to two hours. Again, in the process of Rose, *et al.*, Cr and Pt are deposited on the superalloy in separate steps.

[0008] As can be seen, there is a need for a process for concurrently depositing platinum and a supplementary constituent on a substrate in a single

step. There is a further need for a readily applied Cr containing platinum aluminide coating for superalloy gas turbine engine components. There is a further need for a process for coating superalloy components with a Cr containing platinum aluminide coating, wherein Pt and Cr are deposited on the superalloy surface in a single electrolytic step, such that processing costs are decreased, and productivity is increased. There is also a need for a reliable, stable, effective, and readily available electrolyte composition for co-electrodeposition of Pt and Cr on a substrate.

SUMMARY OF THE INVENTION

[0009] In one aspect of the present invention, there is provided a method for electroplating platinum, including providing a substrate, and electrolytically depositing a metal layer on a surface of the substrate. The metal layer comprises platinum and a supplementary constituent, and the metal layer is deposited from a single electrolyte composition during a single electrolytic step. The electrolyte composition comprises a platinum salt and particles of the supplementary constituent, and the particles of the supplementary constituent are deposited in the metal layer from the electrolyte composition.

[0010] In another aspect of the present invention, there is provided a method for electroplating platinum on a substrate, including electroplating platinum metal on the substrate via an electrolyte comprising particles of one or more supplementary constituents; and, concurrently with electroplating the platinum metal, depositing particles of the one or more supplementary constituents on the substrate. Beneficial supplementary constituents may comprise the following elements, which may be selected for their ability to form protective oxides (Al, Cr), enhance adhesion of protective oxides (Y, Zr, Hf, La, Sc, Si), enhance coating ductility (Ni, Co), enhance coating strength at high temperatures (Ta, Re), and reduce the diffusional interaction with the substrate (Ni, Co, Fe).

[0011] In still another aspect of the present invention, there is provided a process for preparing a coated component, including providing a substrate; electroplating a metal layer on a surface of the substrate, wherein the electroplated metal layer comprises platinum metal and particles of at least one supplementary constituent entrapped within the platinum metal; depositing aluminum on the electroplated metal layer; and forming a platinum aluminide coating on the substrate, wherein the platinum aluminide coating comprises the supplementary constituent. Elements present in the substrate, such as nickel, may be incorporated into the coating during a high-temperature post-plating diffusion heat treatment, high-temperature diffusion aluminizing processing, or post-aluminizing heat treatments. Major elements present within the coating may be Pt, Ni (from the substrate) and Al. Major constituent elements are predominately present in the form of intermetallic phases following aluminizing and heat treatment. In particular, the NiAl phase has solubility for Pt and other elements. Even though Ni may be a major constituent of the coating composition on a Ni-based substrate, the coatings are known in the industry as Pt-aluminides, which refers to the elements that are added during coating processing. We also use the industrial terminology for these coatings.

[0012] In yet another aspect of the present invention, a process for preparing a coated component may include providing a substrate; electroplating a platinum metal layer on the substrate, wherein the platinum metal layer is electrodeposited via an electrolyte composition comprising chromium particles; concurrently with electroplating the platinum metal layer, depositing the chromium particles on the substrate, wherein the chromium particles are entrapped within the platinum metal layer. The process may further include exposing the substrate to a first heat treatment; thereafter, aluminizing the substrate; and exposing the substrate to a second heat treatment to form a platinum aluminide coating on the substrate, wherein the coating comprises a solid solution of chromium within the intermetallic phase comprising Pt and Al. Particles of elemental Cr or Cr-carbides may also be dispersed within the

coating microstructure. Carbon to form a carbide within the coating may be the result of a coating diffusion reaction with a carbon-containing substrate.

[0013] In an additional aspect of the present invention, there is provided a component including a metal substrate, and a platinum aluminide coating disposed on the substrate. The platinum aluminide coating comprises platinum and chromium, wherein the chromium is co-electrodeposited with the platinum, wherein the chromium forms a solid solution within the platinum, and the coating is free from, or substantially free from, chlorine, sulfur, phosphorus, or compounds thereof.

[0014] In a further aspect of the present invention, there is provided a corrosion- and oxidation resistant coating, comprising electrodeposited platinum, and chromium. The chromium is co-electrodeposited with the platinum, the chromium forms a solid solution within the platinum and substrate elements, such as Ni, Co, or Fe, and the coating is free from, or substantially free from, chlorine, sulfur, phosphorus, or compounds thereof.

[0015] In another aspect of the present invention, an electrolyte composition for electrodeposition of platinum comprises a platinum salt, a carbonate or bicarbonate of an alkali metal, and particles of at least one supplementary constituent such as Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

[0016] In yet another aspect of the present invention, an electrolyte composition for electrodeposition of platinum comprises dinitrodiamine platinum, an alkali metal carbonate or bicarbonate, and from about 0.2 to 80 g/L of chromium metal powder.

[0017] These and other features, aspects and advantages of the present invention will become better understood with reference to the following drawings, description and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figure 1A is a sectional view schematically representing a component having a corrosion- and oxidation resistant coating, according to one embodiment of the invention;

[0019] Figure 1B is a sectional view schematically representing a component having a platinum aluminide coating disposed on a substrate, and an additional layer disposed on the platinum aluminide coating, according to another embodiment of the invention;

[0020] Figure 2 schematically represents a series of steps involved in a method for electroplating platinum and a supplementary constituent on a substrate, according to one embodiment of the invention;

[0021] Figure 3 schematically represents a series of steps involved in a method for forming a corrosion- and oxidation resistant coating on a substrate, according to another embodiment of the invention;

[0022] Figure 4 schematically represents a series of steps involved in a method for coating a component, according to the invention;

[0023] Figures 5A-D schematically represent stages in preparing a corrosion- and oxidation protective coating, according to another embodiment of the invention;

[0024] Figure 6A is a scanning electron micrograph of an electroplated chromium containing platinum metal layer on a nickel substrate, according to another embodiment of the invention;

[0025] Figure 6B is an energy-dispersive x-ray spectrum taken from the image area of Figure 6A;

[0026] Figure 7A is a scanning electron micrograph of an electroplated chromium containing platinum metal layer showing a chromium particle entrapped within the electroplated layer, also according to the invention;

[0027] Figure 7B is an energy-dispersive x-ray spectrum taken from the chromium particle shown in Figure 7A, according to the invention;

[0028] Figure 8A is a scanning electron micrograph of an annealed electroplated chromium containing platinum metal layer, also according to the

invention; and

[0029] Figure 8B is an energy-dispersive x-ray line-scan corresponding to the profile of the image area of Figure 8A.

DETAILED DESCRIPTION OF THE INVENTION

[0030] The following detailed description is of the best currently contemplated modes of carrying out the invention. The description is not to be taken in a limiting sense, but is made merely for the purpose of illustrating the general principles of the invention, since the scope of the invention is best defined by the appended claims.

[0031] Broadly, the present invention provides corrosion- and oxidation resistant chromium- and/or reactive element-containing platinum aluminide protective coatings for substrates that are prone to corrosion and oxidation and, in particular, for substrates that are exposed to high temperatures in the range of 600 to 1150°C during service conditions. The reactive element may be a metal such as Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Protective coatings of the instant invention may be applied to a broad range of substrates, including substrates comprising iron-, nickel-, and cobalt-based alloys, such as nickel-based superalloys. Protective coatings of the instant invention may be used in a diverse array of industrial applications where corrosion and oxidation protection of components or substrates is required, including: gas turbine engines used for aircraft propulsion, automotive power, and power generation, as well as chemical processing.

[0032] As a specific example, coatings of the instant invention may be used to protect components such as blades and vanes in the high pressure turbine section of gas turbine engines. Platinum aluminide coatings of the present invention may serve as a stand-alone protective coating. Platinum aluminide coatings of the present invention may also function as a bond coating for deposition of an additional layer, such as a ceramic thermal barrier coating,

directly on the bond coating.

[0033] In general, platinum alloy protective coatings of the instant invention may be formed by a platinum electrodeposition process involving the concurrent electrodeposition of platinum and powder containing one or more supplementary constituents, such as chromium, chromium oxide, a chromium alloy, a reactive element, or an alloy of a reactive element, from a single electrolyte composition to form an electrodeposited metal layer on a substrate to be coated. Pt-aluminide coatings of the instant invention may be formed by subsequent aluminizing the platinum alloy coating and heat treatment.

[0034] In contrast, in prior art platinum aluminide coating processes, platinum and chromium have been deposited in separate steps. As an example, a prior art process for deposition of Pt and Cr disclosed in US Patent No. 5,482,578 involves deposition of a platinum group metal on the superalloy, heating *in vacuo* at about 1900° F for about an hour, diffusion coating the platinum-group metallized superalloy with an Al/Cr powder, and finally heat treating the Al/Cr diffusion coated, metallized superalloy at about 1925° to 2050° F in hydrogen for about one to two hours.

[0035] In further contrast to the prior art, and in one embodiment of the present invention, chromium and platinum constituents of a Cr containing platinum aluminide coating may be electrolytically co-deposited on a substrate surface, in a single step, using an electrolyte composition comprising a platinum salt and Cr metal powder.

[0036] An electrolyte composition of the instant invention may be free from, or substantially free from, sulfur, chlorine, and phosphorus impurities. Moreover, a platinum aluminide coating prepared using such an electrolyte composition may similarly be free from, or substantially free from, sulfur, chlorine, and phosphorus impurities. In contrast, electrolyte compositions used in prior art platinum aluminide coating processes result in the co-deposition of sulfur, chlorine, and phosphorus impurities in the electroplated platinum metal layer. The presence of sulfur, chlorine, and phosphorus impurities reduces the

life of the coating and of the coated component.

[0037] An electrolyte for electroplating superalloy components previously disclosed in commonly assigned US Patent No. 6,306,277 contained the platinum salt, dinitrodiamine platinum, and was substantially free from sulfur, chlorine, and phosphorus impurities. However, in contrast to the instant invention, the electrolyte of the '277 was not described as containing metal particles or chromium.

[0038] Figure 1A is a sectional view schematically representing a component 200, according to one embodiment of the invention. Component 200 may include a substrate 202 and a coating 210 disposed on substrate 202. Coating 210 may be a corrosion resistant protective coating. Coating 210 may also be an oxidation resistant protective coating. Coating 210 may be a stand-alone corrosion- or oxidation resistant coating. Coating 210 may also serve as a bond coating adapted for accepting an additional coating thereon (see, for example, Figure 1B).

[0039] Again with reference to Figure 1A, coating 210 may be a platinum aluminide coating. For example, coating 210 may comprise platinum and aluminum in an intermetallic compound. Coating 210 may further comprise at least one supplementary constituent. The at least one supplementary constituent may include a metal, such as chromium, or an oxide such as chromium oxide, both of which may impart the characteristic of corrosion resistance to coating 210. The at least one supplementary constituent may additionally, or alternatively, include one or more reactive elements, such as Al, Cr, Y, Zr Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. The one or more reactive elements may impart the characteristic of oxidation resistance to coating 210. The one or more reactive elements may further impart, to some extent, the characteristic of corrosion resistance to coating 210. Similarly, the presence of chromium may impart, to some extent, the characteristic of oxidation resistance as well as corrosion resistance to coating 210. The one or more reactive elements may further impart, to some extent, the characteristic of ductility to

coating 210. The one or more reactive elements may further impart, to some extent, the characteristic of high-temperature strength, or resistance to stress-relaxation, to coating 210.

[0040] In some embodiments, the at least one supplementary constituent may comprise a powdered chromium alloy, such as an alloy of chromium with at least one of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Coating 210 may comprise platinum metal and a solid solution of at least one supplementary constituent. For example, after a post-plating heat treatment, coating 210 may be a solid-solution alloy comprising platinum, chromium, and the base-metal. The supplementary constituent, e.g., chromium, may be substantially uniformly distributed within coating 210. The platinum and supplementary constituent(s) of coating 210 may be electrodeposited, e.g., electroplated or electroformed, on substrate 202. As an example, the platinum of coating 210 may be electrodeposited via an electrolyte composition comprising a platinum salt and particles of at least one supplementary constituent. The chromium or other supplementary constituent of coating 210 may be co-electrodeposited with platinum. That is to say, the chromium or other supplementary constituent of coating 210 may be electrodeposited concurrently with electrodeposition of platinum from a single electrolyte composition, during a single electrolytic step.

[0041] The single electrolytic step for co-electrodeposition of chromium and platinum may provide an electroplated layer comprising platinum metal and a plurality of chromium particles entrapped therein. Herein, coatings, compositions, and processes of the invention may be described with reference to chromium, it being understood that in some embodiments other supplementary constituent(s), such as chromium oxide, various chromium alloys, or one or more reactive elements, may be used alternatively, or in addition to, chromium.

[0042] Again with reference to Figure 1A, substrate 202 may comprise an iron-, nickel-, or cobalt-base alloy. For example, the substrate may be a nickel-base superalloy. Component 200 may be a gas turbine engine component,

such as a turbine blade or vane. However, the present invention is not limited to gas turbine engine components, but rather the present invention may find applications wherever corrosion- and/or oxidation resistant coatings are required.

[0043] An electrolyte composition for concurrent deposition of platinum and chromium, according to one aspect of the invention, may comprise the platinum salt, dinitrodiamine platinum ($Pt(NH_3)_2(NO_2)_2$), in an amount typically in the range of from about 1 to 100 g/L, usually from about 5 to 75 g/L, and often from about 25 to 55 g/L.

[0044] The electrolyte composition for concurrent deposition of platinum and chromium may further comprise an alkali metal (Group I element) carbonate or bicarbonate, i.e., M_2CO_3 or $MHCO_3$, wherein M is Li, Na, K, Rb, or Cs. The alkali metal carbonate or bicarbonate may be present in an amount typically in the range of from about 1 to 200 g/L, usually from about 10 to 175 g/L, and often from about 50 to 150 g/L. The electrolyte composition may be prepared by adding the platinum salt and the alkali metal carbonate or bicarbonate to water.

[0045] The electrolyte composition for concurrent deposition of platinum and chromium may further comprise particles of at least one supplementary constituent. As an example, the electrolyte composition for concurrent deposition of platinum and chromium may comprise chromium metal powder. The particles of chromium metal powder in the electrolyte composition may have a mean diameter in the range of from about 1 to 50 microns, usually from about 1 to 20 microns, and often from about 1 to 10 microns. The electrolyte composition for the concurrent deposition of platinum and chromium may comprise particles in the range of from about 0.2 to 400 g/L, usually from about 0.2 to 50 g/L, and often from about 1 to 20 g/L. Chromium powder may be alloyed with one or more supplementary constituents. Alternatively, an electrolyte composition for concurrent deposition of platinum and one or more supplementary constituents may include particles consisting entirely of one or

more supplementary constituents other than chromium.

[0046] The electrolyte composition for concurrent deposition of platinum and chromium may be free from, or substantially free from, chlorine (Cl), sulfur (S), phosphorus (P), or compounds thereof. For example, the electrolyte composition may comprise from zero to trace quantities of sulfur, chlorine, and phosphorus. Similarly, coating 210 prepared from co-electrodeposited Pt and Cr according to the present invention may be free from, or substantially free from, chlorine (Cl), sulfur (S), phosphorus (P), or compounds thereof.

[0047] After aluminizing and heat treatment have been completed, platinum aluminide coating 210 may have a thickness in the range of from about 5 to 100 microns, typically in the range of from about 10 to 70 microns, and usually in the range of from about 20 to 50 microns.

[0048] Figure 1B is a sectional view schematically representing a component 200', according to another embodiment of the invention. Component 200' may include a substrate 202 and a coating 210' disposed on substrate 202. Coating 210' may have the same, or similar, characteristics and features as described herein for coating 210 (Figure 1A). Similarly, coating 210' may be formed using the same, or similar, processes as for forming coating 210.

[0049] Coating 210' may serve as a platinum aluminide bond coating, and component 200' may further include an additional layer 220 disposed on bond coating 210'. As an example, additional layer 220 may be a columnar, ceramic thermal barrier coating. Such a thermal barrier coating may comprise a stabilized zirconia, such as an yttria stabilized zirconia. A columnar, ceramic thermal barrier coating is disclosed in commonly assigned, co-pending U.S. Patent Application Serial No. 10/621,981, filed July 16, 2003 (entitled: *Thermal Barrier Coating with Stabilized Compliant Microstructure*), the disclosure of which is incorporated by reference herein in its entirety.

[0050] Figure 2 schematically represents a series of steps involved in a method 300 for electroplating platinum and a supplementary constituent on a

substrate, according to one embodiment of the invention. Step 302 may involve providing a substrate. The substrate may comprise iron-, nickel-, or a cobalt-base alloy. The substrate may be a nickel-based superalloy, e.g., a superalloy for a gas turbine engine component.

[0051] Step 304 may involve providing an electrolyte composition. The electrolyte composition may have characteristics and constituents as described hereinabove. For example, the electrolyte composition may include a platinum salt, an alkali metal carbonate or bicarbonate, and particles of one or more supplementary constituent(s). The supplementary constituent(s) may comprise particles in the form of a metal powder or metal oxide powder. The one or more supplementary constituents may include a corrosion resistant material, such as chromium metal, chromium oxide, and/or Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. As an example, the one or more supplementary constituents may comprise a mixture of chromium powder, or chromium oxide powder, with elemental or alloyed particles of a reactive element such Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In some embodiments, the electrolyte composition may include a supplementary constituent comprising a chromium alloy, wherein the chromium alloy comprises chromium and one or more reactive elements such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Quantitative data on the composition of an electrolyte of the instant invention are provided elsewhere herein.

[0052] Again with reference to Figure 2, step 306 may involve electrodepositing platinum metal on the substrate and, at the same time, depositing at least one supplementary constituent on the substrate surface, via the electrolyte provided in step 304. That is to say, according to the instant invention, particles of a supplementary constituent, such as chromium, chromium oxide, a reactive element, or a chromium alloy, may be electrodeposited concurrently with electrodeposition of platinum in a single electrolytic step (e.g., step 306 of method 300) from a single electrolyte composition. The reactive element may be a metal or alloy comprising Al, Cr,

Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Prior to step 306, the substrate may be prepared by grit blasting or mechanically polishing the substrate surface to be coated. The substrate may be further prepared by chemical activation, for example, by exposure to HCl.

[0053] The electrolyte composition may be agitated or sonicated prior to step 306. The electrolyte composition may be stirred during step 306. Accordingly, during step 306 particles of the one or more supplementary constituents may be maintained in suspension.

[0054] Step 306 may involve applying a voltage between the substrate (cathode) and one or more anodes. The one or more anodes may each comprise platinum. The voltage between the substrate and the one or more anodes may be in the range of from about 1.2 to 2.2 volts, usually from about 1.5 to 2.0 volts, and often from about 1.7 to 1.9 volts. The current density per unit area of the substrate may be in the range of from about 2.0 to 3.0 $A.dm^{-2}$. During step 306, the electrolyte composition may be maintained at a temperature in the range of from about 60 to 100° C, usually from about 75 to 95° C, and often from about 82 to 86° C.

[0055] In step 308, the substrate and the electrodeposited layer formed during step 306 may be heated or annealed. For example, heat may be applied to promote bonding of the electrodeposited layer to the substrate surface, or to interdiffuse constituents of the electrodeposited layer with the surface layer of the substrate.

[0056] In some embodiments, step 308 may involve performing a first heat treatment, or annealing, the substrate. The first heat treatment may be performed at a relatively low temperature sufficient to promote bonding of the electrodeposited layer to the substrate surface. A temperature in the range of from about 300 to 650° C may be sufficient to promote such bonding of the electrodeposited layer to the substrate surface. The coating after heat treatment in the above range may still consist of platinum and particles of the supplementary constituent material.

[0057] Alternatively, the heat treatment of step 308 may be performed at a relatively high temperature sufficient to promote interdiffusion of constituents of the electrodeposited layer with the adjacent surface layer of the substrate surface. A temperature in the range of from about 1000 to 1100° C may be sufficient to promote such diffusion of constituents of the electrodeposited layer and the substrate. When a heat treatment in the 1000 to 1100° C range is performed, the resulting coating may comprise a solid solution alloy; e.g., the coating may comprise a metallic solid solution of Ni, Pt and Cr when the substrate is a nickel-base alloy.

[0058] Step 308 may be performed, for a period in the range of from about 15 minutes to four (4) hours, in a protective atmosphere (e.g., in argon), or under vacuum.

[0059] Figure 3 schematically represents a series of steps involved in a method 400 for forming a corrosion- and oxidation resistant coating on a substrate, according to another embodiment of the invention. Step 402 may involve providing a substrate, generally as described hereinabove with respect to step 302, method 300 (Figure 2).

[0060] Step 404 may involve concurrently depositing platinum metal and at least one supplementary constituent on the substrate surface, via a single electrolyte composition. The electrolyte may have the composition and characteristics described hereinabove. For example, the electrolyte may comprise a platinum salt and particles of one or more supplementary constituents, such as chromium, chromium oxide, Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re, or a chromium alloy. Such an alloy of chromium may include one or more metals such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Step 404 may be performed generally as described hereinabove with respect to step 306, method 300 (Figure 2).

[0061] Step 404 may result in the formation of a metal layer comprising platinum metal and particles of a supplementary constituent, e.g., chromium particles, embedded or entrapped within the platinum metal (see, e.g., Figures

6A-B, 7A-B).

[0062] Step 406 may be similar to step 308 as described hereinabove with reference to method 300 (Figure 2). In some embodiments, step 406 may involve performing a first heat treatment, or annealing, the substrate. The first heat treatment may be performed at a relatively low temperature sufficient to promote bonding of the electrodeposited layer to the substrate surface. A temperature in the range of from about 550 to 650° C may be sufficient to promote such bonding of the electrodeposited layer to the substrate surface.

[0063] Alternatively, the first heat treatment may be performed at a relatively high temperature sufficient to promote interdiffusion of constituents of the electrodeposited layer with the adjacent surface layer of the substrate surface. A temperature in the range of from about 1000 to 1100° C may be sufficient to promote such diffusion of constituents of the electrodeposited layer and the substrate. When a heat treatment in the 1000 to 1100° C range is performed, the resulting coating may comprise a solid solution alloy; e.g., the coating may comprise a metallic solid solution of Ni, Pt and Cr when the substrate is a nickel-base alloy. Step 406 may be performed, for a period in the range of from about 15 minutes to four (4) hours, in a protective atmosphere (e.g., in argon), or under vacuum. In some embodiments, step 406 may be omitted.

[0064] Step 408 may involve depositing aluminum on the substrate or electrodeposited layer. The aluminum may be deposited on the substrate using various techniques known in the art, such as chemical vapor deposition (CVD), above the pack, pack aluminizing, physical vapor deposition, or as an aluminum powder slurry. Depending on the deposition technique, step 408 may typically be performed at a temperature in the range of from room temperature to 1100° C. Aluminizing processes conducted above about 800°C may promote interdiffusion of coating elements with the surface layer of the substrate.

[0065] Step 410 may involve performing a second heat treatment on the substrate to form a coating on the substrate. The coating may comprise a

platinum aluminide and one or more supplementary constituents. The supplementary constituent(s) may comprise chromium or chromium oxide. The supplementary constituent(s) may alternatively comprise one or more reactive elements, such Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In some embodiments, the supplementary constituent(s) may comprise chromium or chromium oxide, and may further comprise one or more of the reactive elements, such Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In other embodiments, the supplementary metal element(s) may comprise a chromium alloy comprising one or more metals such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. Step 410 may be performed in a protective atmosphere (e.g., in argon), or under vacuum.

[0066] The coating formed according to method 400 may have those characteristics, features and elements as described hereinabove, for example, with reference to Figures 1A-B. Thus, the coating formed according to method 400 may serve as a corrosion resistant coating. The coating may also serve as an oxidation resistant coating.

[0067] Step 410 may be performed at a relatively high temperature sufficient to promote interdiffusion of constituents of the electrodeposited layer, the aluminum-rich layer, and the surface layer of the substrate. For example, the second heat treatment may be performed at a temperature sufficient to promote diffusion of aluminum with the electrodeposited platinum and chromium, and nickel from the surface layer of a superalloy substrate. Step 410 may be performed at a temperature in the range of from about 1000 to 1100° C, and for a period in the range of from about 15 minutes to four (4) hours. The resulting heat-treated coating may typically comprise a high melting temperature matrix phase, such as (Pt, Ni) Al intermetallic phase, which has finite solubility for the supplementary constituents. Chromium solubility within the (Pt, Ni) Al matrix phase may be limited to a few percent. Excess chromium may be present as discrete particles within the coating.

[0068] In contrast to certain line-of-sight deposition and coating

techniques of the prior art, methods and processes of the instant invention, for example method 400, can be used to form a uniform coating on substrates having complex geometry.

[0069] Figure 4 schematically represents a series of steps involved in a method 500 for coating a component, according to another embodiment of the invention. Step 502 may involve providing a substrate, for example, generally as described hereinabove with respect to step 302, method 300. Step 504 may involve forming a bond coating on the substrate. The bond coating formed in step 504 may be a platinum aluminide coating comprising platinum metal and chromium or a supplementary constituent that enhances oxide scale adhesion, such as Y, Zr, Hf, La, or Sc. The bond coating formed in step 504 may be formed generally as described hereinabove for steps 404 through 410 of method 400 (Figure 3).

[0070] Step 506 may involve forming an additional layer on the bond coating. In some embodiments, the additional layer formed in step 506 may be a thermal barrier coating. As an example, a thermal barrier coating formed on the bond coating may comprise a stabilized zirconia, such as an yttria stabilized zirconia. A thermal barrier coating formed on the bond coating may be deposited by various deposition processes known in the art, such as electron beam physical vapor deposition (EB-PVD) or a plasma spray process. A thermal barrier coating is disclosed in commonly assigned, co-pending U.S. Patent Application Serial No. 10/621,981, filed July 16, 2003 (entitled: *Thermal Barrier Coating with Stabilized Compliant Microstructure*), the disclosure of which is incorporated by reference herein in its entirety.

[0071] Figures 5A-D schematically represent stages in preparing a corrosion- and/or oxidation protective coating, according to one embodiment of the instant invention. Figure 5A represents a substrate 202 as seen in cross-section. Figure 5B represents substrate 202 having an electrodeposited layer 204 disposed thereon. Electrodeposited layer 204 may comprise electrodeposited platinum metal, together with entrapped particles of a

supplementary constituent. The supplementary constituent may comprise particles of chromium or chromium oxide. The supplementary constituent may further comprise particles of a reactive element such as Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. In some embodiments, the supplementary constituent may comprise particles of an alloy comprising chromium and one or more of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re. According to one aspect of the invention, electrodeposited layer 204 may be deposited in a single electrolytic step via an electrolyte composition comprising a platinum salt and particles of a suspended supplementary constituent.

[0072] Figure 5C represents an aluminized substrate 202 having an aluminum layer 206 deposited on electrodeposited layer 204. Figure 5D represents a platinum aluminide coating 210 on substrate 202. Platinum aluminide coating 210 may be formed from electrodeposited layer 204, and aluminum layer 206, and the surface layer of the substrate following heat treatment. The heat treatment may be sufficient to interdiffuse at least a portion of electrodeposited layer 204 and aluminum layer 206 with the surface layer of substrate 202. The heat treatment may also be sufficient to dissolve entrapped particles of a supplementary constituent (e.g., chromium), permitting it to become a constituent in the intermetallic solid solution matrix phase of the platinum aluminide coating.

EXAMPLES

Example 1

[0073] A solution comprising 12 g/L Pt and 100 g/L Na_2CO_3 was prepared by dissolving 40 g dinitrodiamine platinum ($Pt(NH_3)_2NO_2)_2$) (60.0 % Pt), and 200 g Na_2CO_3, in 2 L water. Electrolyte compositions were prepared from the solution by adding various amounts of Cr metal powder (Reade Advanced Materials, Providence, Rhode Island USA) to the dinitrodiamine

Pt/Na_2CO_3 solution. The Cr metal powder had a particle size of about 4 microns.

[0074] A nickel (Ni) sheet 2.54 cm x 1.27 cm x 0.080 cm (6.5 cm^2) was mechanically polished and chemically activated in 18% HCl for 1 min (per ASTM B558-79, 4.6). The Ni sheet was electroplated for 1 h using 2 Pt anodes at a voltage of 1.80 V, current density 2.0-2.9 A/dm^2, at a bath temperature of 82 to 86° C with magnetic stirring of the electrolyte.

Example 2

[0075] A Cr containing Pt metal layer (Pt + Cr layer) was electrodeposited on a Ni sheet from a Pt electrolyte composition (prepared according to Example 1) containing 10 g/L Cr metal powder. The weight of the Ni sheet prior to plating was 2.161 g. The weight of the Ni sheet with the Pt + Cr electroplated layer was 2.282 g. The weight of the Pt + Cr electroplated layer was 0.121 g. The thickness of the Pt + Cr electroplated layer was calculated from weight gain to be 8.7 microns, assuming that the electroplated layer consists of pure Pt.

Example 3

[0076] A Ni sheet electroplated with a Cr containing platinum (Pt + Cr) layer was annealed at 600° C for 30 min in argon. A scanning electron micrograph (original magnification, 2,500X) of a polished section of the Pt + Cr electroplated layer 204 is shown in Figure 6A. Cr particles, entrapped within the volume of the Pt metal of the electroplated layer, are clearly visible. No gaps are visible around the Cr particles. Similarly, there appears to be good bonding between the Pt and Ni substrate. The thickness of the Pt + Cr electroplated layer is mostly less than about 10 microns. Figure 6B is an energy-dispersive x-ray (EDX) spectrum taken from the image area of Figure 6A, indicating elemental x-ray peaks for Pt, Cr, and Ni.

[0077] Figure 7A is a higher magnification scanning electron micrograph (original magnification, 20,000X) of a polished section of the Pt + Cr electroplated layer. Figure 7A clearly shows a Cr particle entrapped within the Pt metal of the electroplated layer. Figure 7B is an energy-dispersive x-ray (EDX) spectrum taken from the Cr particle shown in Figure 7A. Figure 7B indicates elemental x-ray peaks for Cr and Pt.

Example 4

[0078] A Ni sheet electroplated with a Cr containing platinum (Pt + Cr) layer as described hereinabove was heat treated at 1065° C for 60 min in argon. A scanning electron micrograph (original magnification, 1,500X) of the Pt + Cr electroplated layer after heat treatment is shown in Figure 8A. Cr particles are no longer visible, indicating that heat treatment at 1065° C for 60 min may be sufficient to diffuse or dissolve the Cr, as well as the surface of the nickel substrate, into the platinum metal.

[0079] Figure 8B is an energy-dispersive x-ray (EDX) line-scan corresponding to the profile of the image area of Figure 8A. Figure 8B shows the elemental x-ray profile for Pt, Cr, and Ni from the surface of the electroplated and annealed layer to the Ni substrate. It can be seen that, in the region of the electroplated layer/substrate interface, the Pt concentration decreases and the Ni concentration increases with increasing distance from the surface. The concentration of Cr remains approximately constant until the Pt level begins to decline.

[0080] It should be understood, of course, that the foregoing relates to preferred embodiments of the invention and that modifications may be made without departing from the spirit and scope of the invention as set forth in the following claims.

WE CLAIM:

1. A method for electroplating platinum, comprising:

a) providing a substrate; and

b) electrolytically depositing a metal layer on a surface of said substrate, wherein said metal layer comprises platinum and a supplementary constituent,

wherein said metal layer is deposited from a single electrolyte composition during a single electrolytic step,

wherein said electrolyte composition comprises a platinum salt and particles of said supplementary constituent, and

wherein said particles of said supplementary constituent are deposited in said metal layer from said electrolyte composition.

2. The method of claim 1, wherein said supplementary constituent comprises at least one element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

3. The method of claim 1, wherein said supplementary constituent comprises chromium oxide or chromium.

4. The method of claim 1, wherein said supplementary constituent comprises chromium oxide, and at least one reactive element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

5. The method of claim 1, wherein said supplementary constituent comprises a chromium alloy including at least one metal selected from the group consisting of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

6. The method of claim 1, wherein said particles of said supplementary constituent have a mean diameter of from about 1 to 50 microns.

7. The method of claim 1, wherein said particles of said supplementary constituent comprise a mixture of chromium powder and particles of at least one reactive element selected from the group consisting of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

8. The method of claim 1, wherein said substrate comprises an alloy, and the method further comprises:

c) after said step b), aluminizing said substrate; and

d) heating said substrate to form an intermetallic matrix coating, wherein said intermetallic matrix coating comprises platinum, aluminum, said supplementary constituent, and constituents of said alloy substrate.

9. The method of claim 1, wherein said electrolytically deposited metal layer forms a coating on a surface of said substrate, said coating comprising said supplementary constituent, and said substrate comprising an alloy, and the method further comprising:

after said step b), heat treating said coating and said substrate surface to form a metallic solid solution comprising platinum metal, said supplementary constituent, and constituents of said substrate.

10. A method for electroplating platinum on a substrate, comprising:

a) electroplating platinum metal on said substrate via an electrolyte comprising particles of a supplementary constituent; and

b) concurrently with said step a), depositing said particles of said supplementary constituent on said substrate,

wherein said supplementary constituent is selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

11. The method of claim 10, wherein said particles of said supplementary constituent are entrapped within said platinum metal.

12. The method of claim 10, wherein said particles of said supplementary constituent comprise chromium metal powder.

13. The method of claim 10, wherein said electrolyte comprises dinitrodiamine platinum.

14. The method of claim 10, wherein said step a) comprises applying a voltage of from about 1.2 to 2.2 volts between said substrate and an anode.

15. A process for preparing a coated component, comprising:

a) providing a substrate;

b) electroplating a metal layer on a surface of said substrate, wherein said electroplated metal layer comprises platinum metal and particles of at least one supplementary constituent entrapped within said platinum metal, wherein said at least one supplementary constituent is selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni; Co, Fe, Ta, and Re;

c) depositing aluminum on said electroplated metal layer; and

d) forming a platinum aluminide coating on said substrate, wherein said platinum aluminide coating comprises said at least one supplementary constituent.

16. The process of claim 15, wherein said particles and said platinum metal are co-deposited from a single electrolyte composition, and said electrolyte composition comprising said particles.

17. The process of claim 16, further comprising:

e) during said step b), maintaining said particles in suspension.

18. The process of claim 16, wherein said electrolyte composition comprises from about 0.2 to 400 g/L of said particles, and wherein said particles comprise chromium metal powder.

19. The process of claim 15, further comprising:

f) after said step b) and prior to said step c), heating said substrate.

20. The process of claim 19, wherein said step f) comprises heating said substrate to a temperature sufficient to bond said electroplated metal layer to said substrate.

21. The process of claim 20, wherein said temperature sufficient to bond said electroplated metal layer to said substrate is in the range of from about 300 to 650° C.

22. The process of claim 19, wherein said step f) comprises heating said substrate to a temperature sufficient to interdiffuse at least a portion of said electroplated metal layer with said substrate.

23. The process of claim 22, wherein said temperature sufficient to interdiffuse at least a portion of said electroplated metal layer with said substrate is in the range of from about 1000 to 1100° C.

24. The process of claim 15, wherein said substrate comprises an alloy, and wherein said step d) comprises heating said substrate to a temperature sufficient to form said platinum-aluminide coating from said platinum metal, said particles of said at least one supplementary constituent, and constituents of said substrate, wherein said platinum-aluminide coating comprises an intermetallic or metallic solid solution phase, wherein said intermetallic or metallic solid solution phase comprises Pt, Al, said at least one supplementary constituent, and said constituents of said substrate.

25. The process of claim 15, wherein said step d) comprises heating said substrate to a temperature in the range of from about 1000 to 1100° C.

26. A coating for a substrate, said coating prepared according to the process of claim 11.

27. A process for preparing a coated component, comprising:

a) providing a substrate;

b) electroplating a platinum metal layer on said substrate, wherein said platinum metal layer is electrodeposited via an electrolyte composition comprising chromium particles;

c) concurrently with said step b), depositing said chromium particles on said substrate, wherein said chromium particles are entrapped within said platinum metal layer;

d) optionally, exposing said substrate to a first heat treatment;

e) thereafter, aluminizing said substrate; and

f) exposing said substrate to a second heat treatment to form a platinum aluminide coating on said substrate, wherein said platinum aluminide coating comprises:

chromium within an intermetallic solid solution phase, and

said chromium particles dispersed within said intermetallic solid solution phase.

28. The process of claim 27, wherein said electrolyte composition further comprises dinitrodiamine platinum.

29. The process of claim 27, wherein said electrolyte composition further comprises at least one reactive element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

30. The process of claim 27, further comprising:

g) during said step b), stirring said electrolyte composition to maintain said chromium particles in suspension.

31. A component comprising:

a metal substrate; and

a platinum aluminide coating disposed on said substrate, wherein said platinum aluminide coating comprises platinum and a supplementary constituent comprising at least one element selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re,

wherein said supplementary constituent is co-electrodeposited with said platinum,

wherein during a heat treatment said supplementary constituent at least partially dissolves and is incorporated into an intermetallic phase or at least one solid solution phase,

wherein said intermetallic phase or said at least one solid solution phase is formed by reaction of said platinum, said aluminum, and constituents of said metal substrate, and

wherein said coating is substantially free from chlorine, sulfur, phosphorus, or compounds thereof.

32. The component of claim 31, wherein:

said platinum aluminide coating comprises a bond coating, and

said component further comprises a thermal barrier coating disposed on said bond coating.

33. The component of claim 32, wherein said thermal barrier coating comprises a stabilized zirconia.

34. The component of claim 31, wherein said substrate comprises iron-, nickel-, or cobalt-base alloys or a nickel-base superalloy.

35. The component of claim 31, wherein said substrate comprises a blade or vane for a gas turbine engine.

36. A corrosion and oxidation resistant coating, comprising:

electrodeposited platinum;

a supplementary constituent, wherein said supplementary constituent is co-electrodeposited with said platinum; and

deposited aluminum;

wherein said corrosion- and oxidation resistant coating comprises a platinum aluminide coating, said platinum aluminide coating consisting primarily of at least one intermetallic solid solution phase, and

wherein said supplementary constituent is chromium, and wherein said coating is substantially free from chlorine, sulfur, phosphorus, or compounds thereof.

37. The coating of claim 36, wherein said coating has a thickness in the range of from about 5 to 100 microns.

38. The coating of claim 36, wherein said coating comprises from about 2 to 35 weight % chromium.

39. The coating of claim 36, wherein said coating comprises from about 15 to 25 weight % chromium, and from about 10 to 30 weight % aluminum.

40. An electrolyte composition for electrodeposition of platinum, comprising:

a platinum salt;

a carbonate or bicarbonate of an alkali metal; and

particles of at least one supplementary constituent, wherein said at least one supplementary constituent is selected from the group consisting of chromium, chromium oxide, a chromium alloy, and a reactive element, and wherein said reactive element is selected from the group consisting of Al, Cr, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

41. The electrolyte of claim 40, wherein said platinum salt comprises dinitrodiamine platinum, and wherein said electrolyte is substantially free from chlorine, sulfur, phosphorus, or compounds thereof.

42. The electrolyte of claim 40, wherein said at least one supplementary constituent comprises from about 0.1 to 80 g/L, and wherein said particles have a mean diameter in the range of from about 1 to 50 microns.

43. An electrolyte composition for electrodeposition of platinum, comprising:

dinitrodiamine platinum;

an alkali metal carbonate or bicarbonate; and

chromium metal powder in an amount of from about 0.2 to 80 g/L.

44. The electrolyte of claim 43, wherein said dinitrodiamine platinum comprises from about 25 to 55 g/L.

45. The electrolyte of claim 43, wherein said alkali metal carbonate or bicarbonate comprises from about 1 to 200 g/L.

46. The electrolyte of claim 43, wherein said chromium metal powder comprises chromium particles having a mean diameter in the range of from about 1 to 50 microns.

47. The electrolyte of claim 43, further comprising particles of at least one reactive element selected from the group consisting of Al, Y, Zr, Hf, La, Sc, Si, Ni, Co, Fe, Ta, and Re.

48. The electrolyte of claim 47, wherein said reactive element is selected from the group consisting of Y, Zr, Hf, La, and Sc.

PLATINUM ALUMINIDE COATING & METHOD THEREOF

ABSTRACT OF THE DISCLOSURE

Platinum containing coatings for corrosion and oxidation protection of a substrate, and platinum electrodeposition methods for coating a substrate. The coating may comprise platinum and at least one supplementary constituent, and the method may involve co-electrodeposition of platinum and the supplementary constituent from a single electrolyte composition. The supplementary constituent may comprise chromium, an oxidation protective reactive element, or an alloy of chromium with a reactive element. Components protected by such coatings are also disclosed.

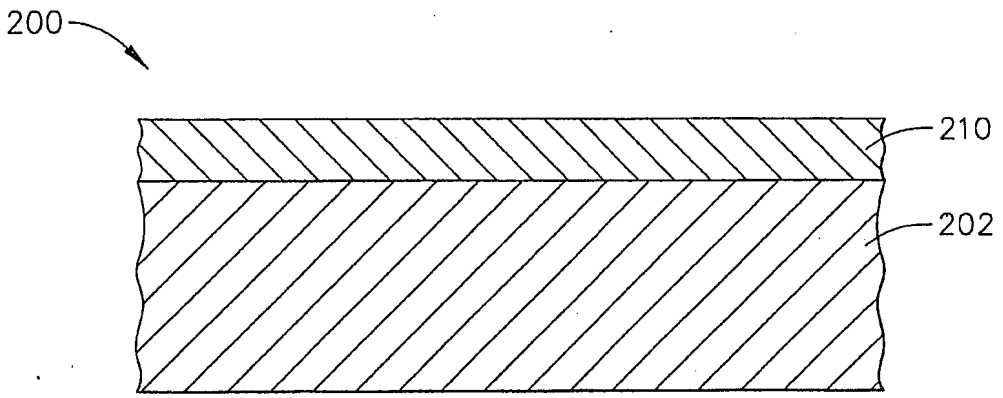

FIG. 1A

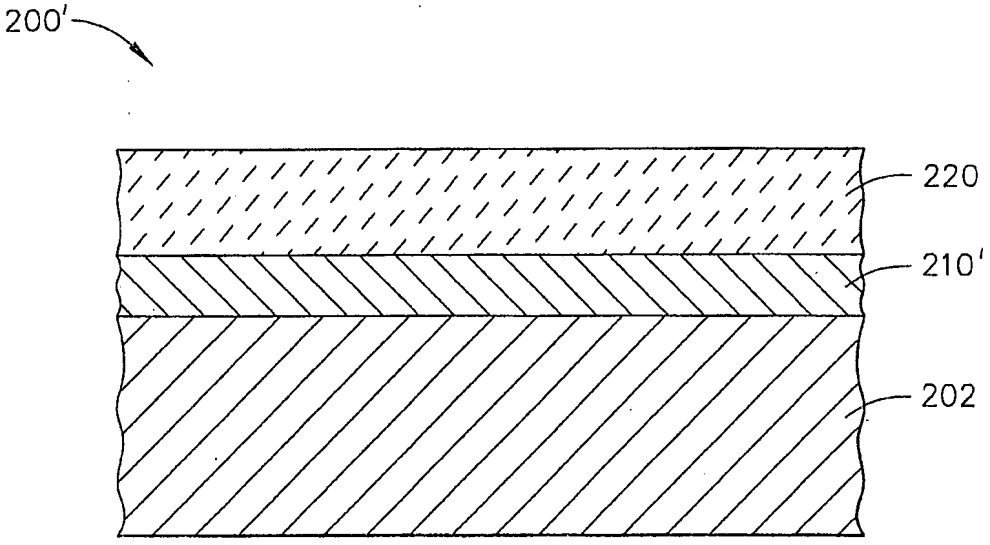

FIG. 1B

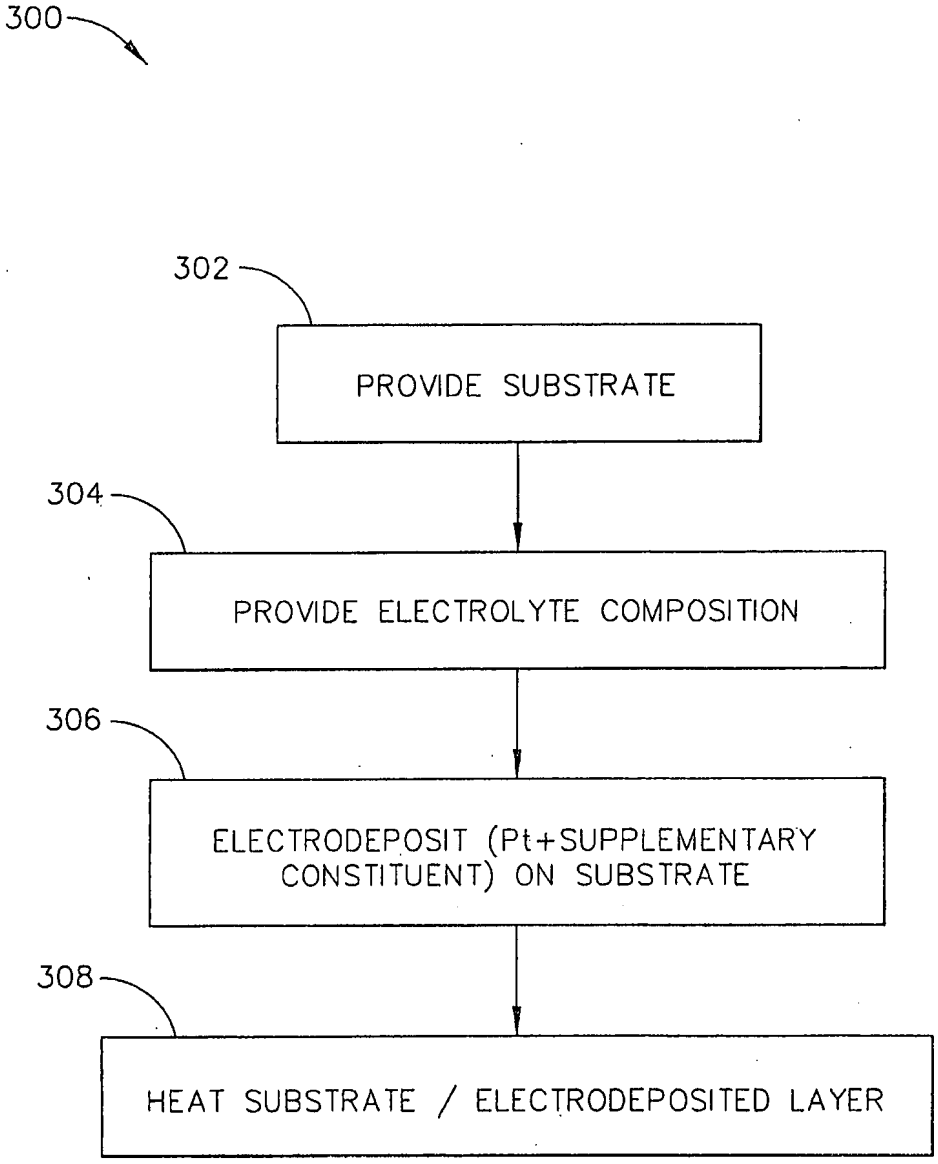
300
302
PROVIDE SUBSTRATE
304
PROVIDE ELECTROLYTE COMPOSITION
306
ELECTRODEPOSIT (Pt+SUPPLEMENTARY CONSTITUENT) ON SUBSTRATE
308
HEAT SUBSTRATE / ELECTRODEPOSITED LAYER

FIG. 2

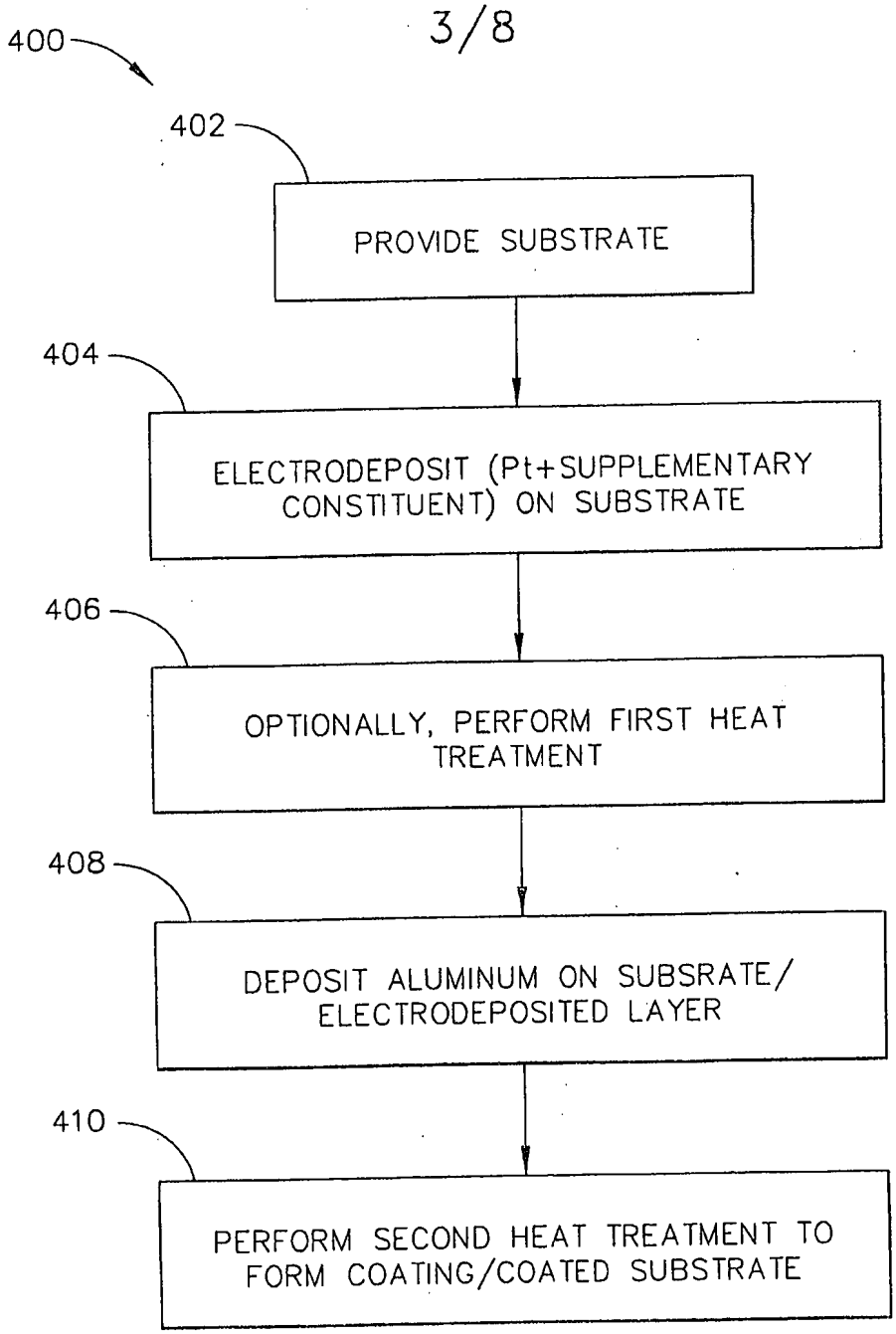
400
402
PROVIDE SUBSTRATE
404
ELECTRODEPOSIT (Pt+SUPPLEMENTARY CONSTITUENT) ON SUBSTRATE
406
OPTIONALLY, PERFORM FIRST HEAT TREATMENT
408
DEPOSIT ALUMINUM ON SUBSRATE/ ELECTRODEPOSITED LAYER
410
PERFORM SECOND HEAT TREATMENT TO FORM COATING/COATED SUBSTRATE

FIG. 3

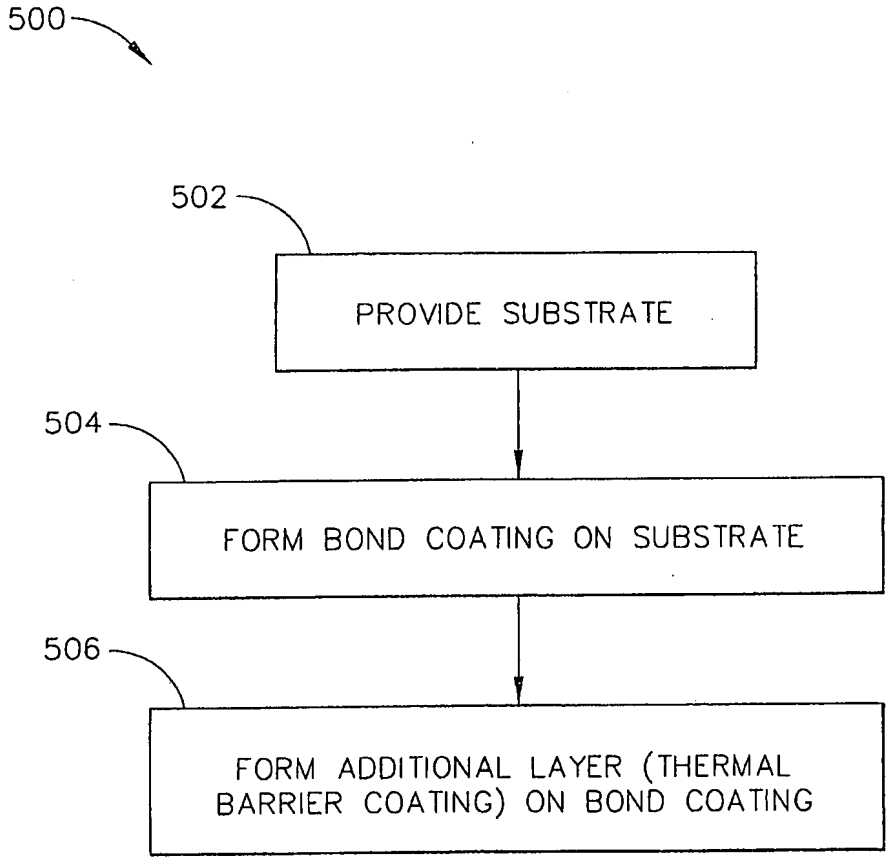
500
502
PROVIDE SUBSTRATE
504
FORM BOND COATING ON SUBSTRATE
506
FORM ADDITIONAL LAYER (THERMAL BARRIER COATING) ON BOND COATING

FIG. 4

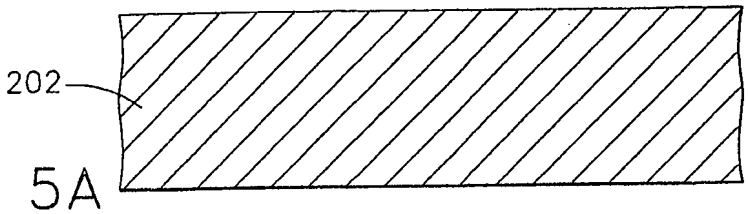

FIG. 5A

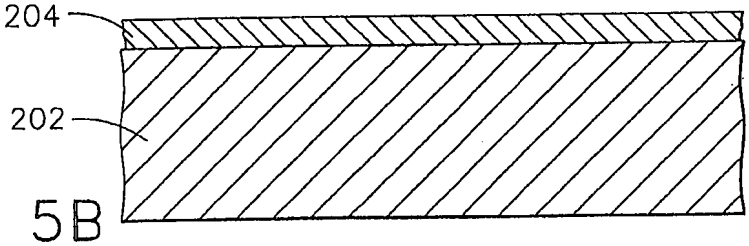

FIG. 5B

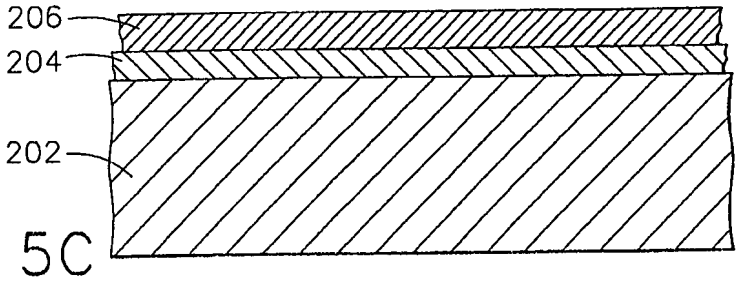

FIG. 5C

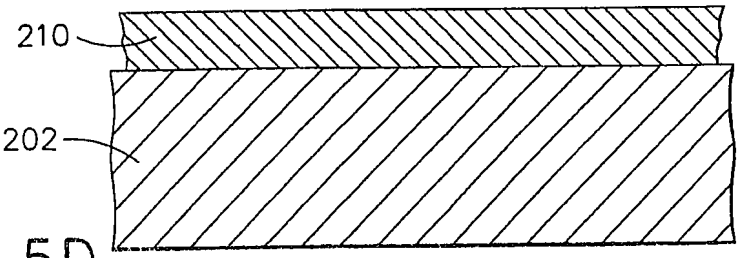

FIG. 5D

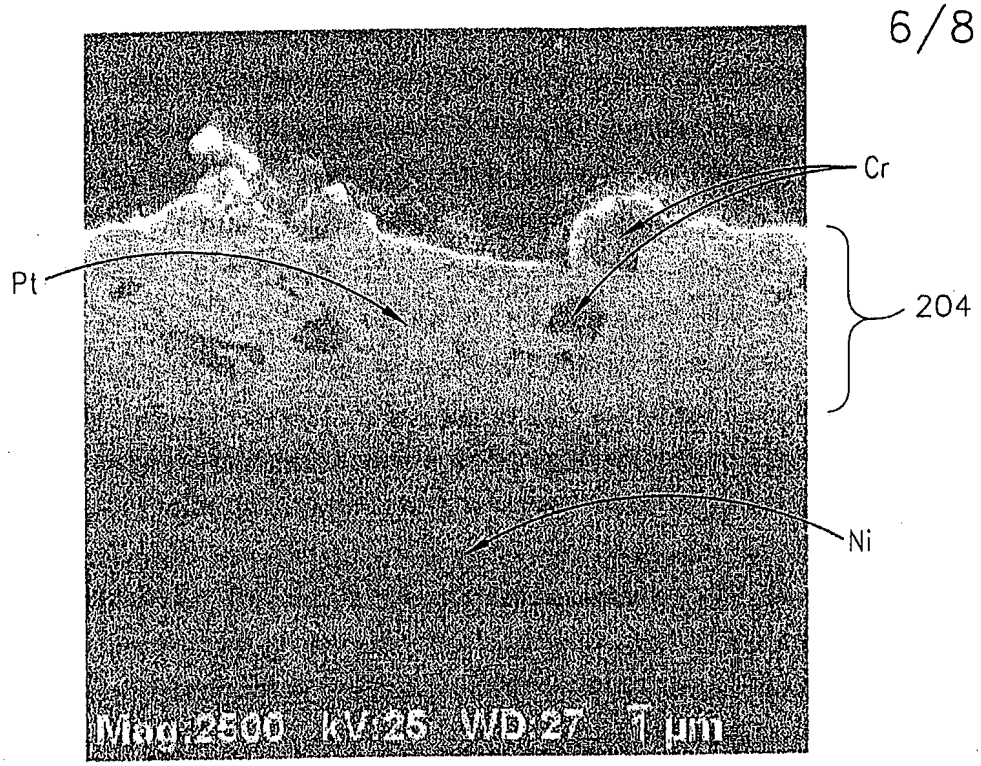
Cr
Pt
204
Ni
Mag 2500 kV 25 WD 27 1 µm

FIG. 6A

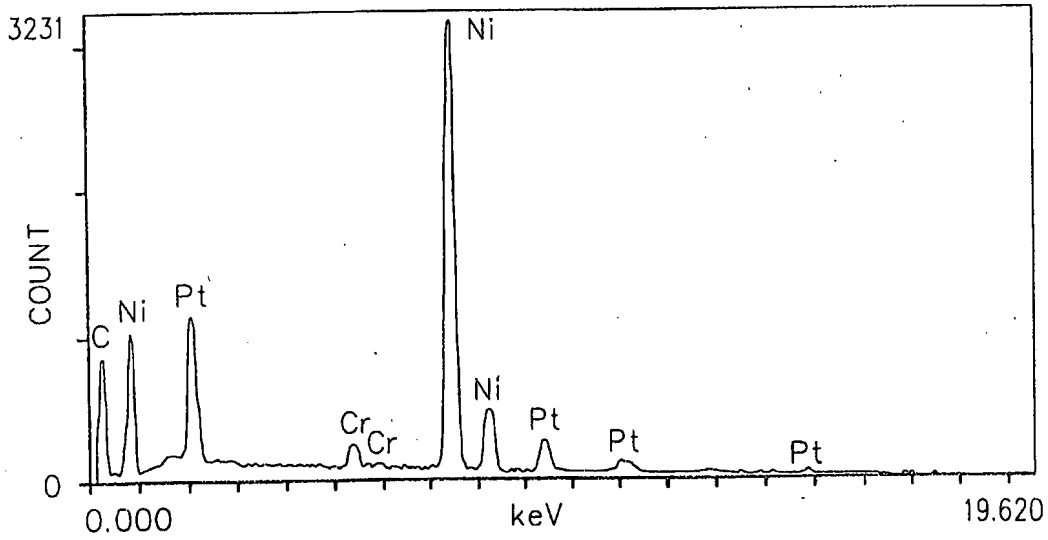
3231
Ni
COUNT
C
Ni
Pt
Cr
Cr
Ni
Pt
Pt
Pt
0
0.000
keV
19.620

FIG. 6B

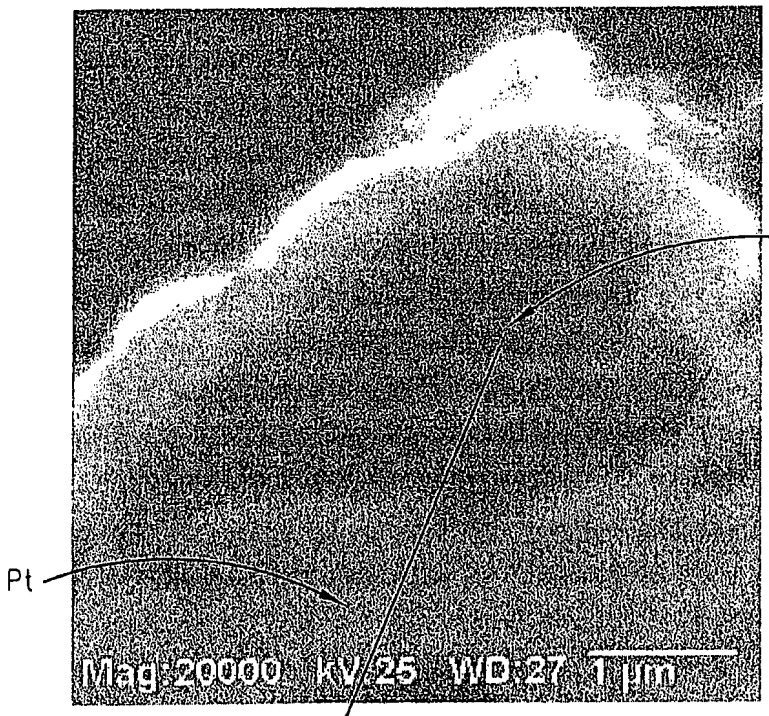
Cr
Pt
Mag 20000 kV 25 WD 27 1 µm

FIG. 7A

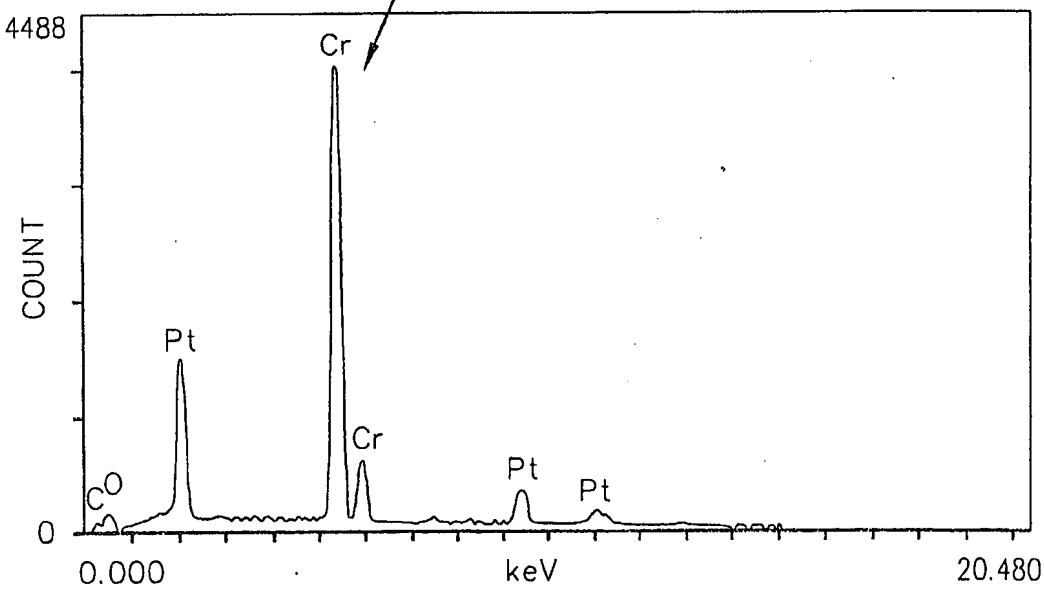
4488
Cr
COUNT
Pt
Cr
Pt
Pt
C
O
0
0.000
keV
20.480

FIG. 7B

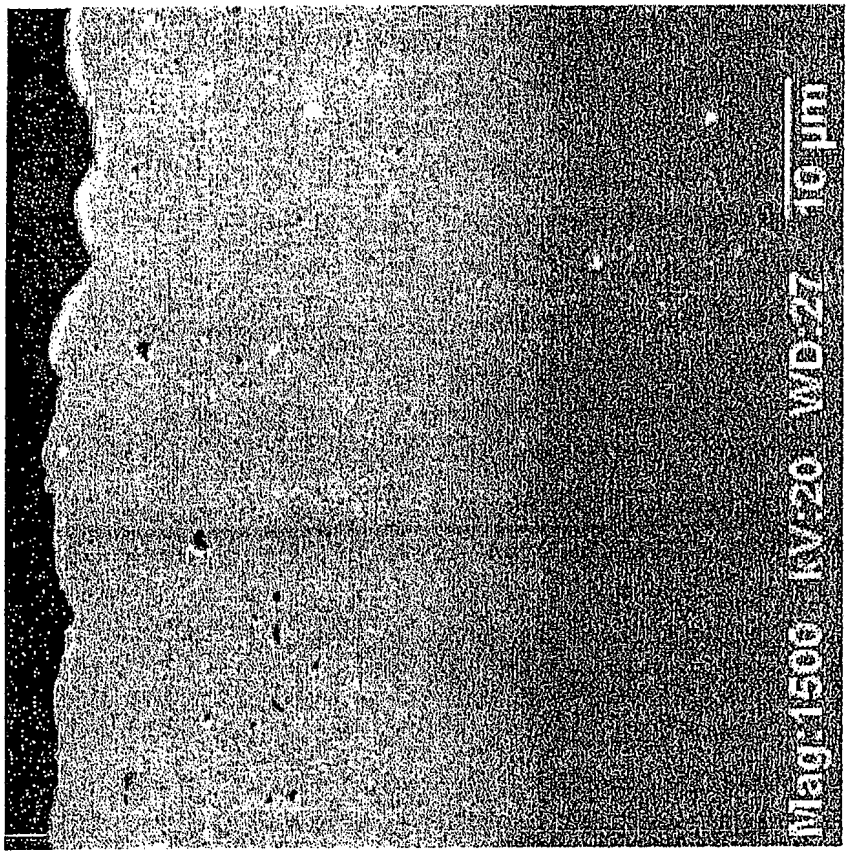

FIG. 8A

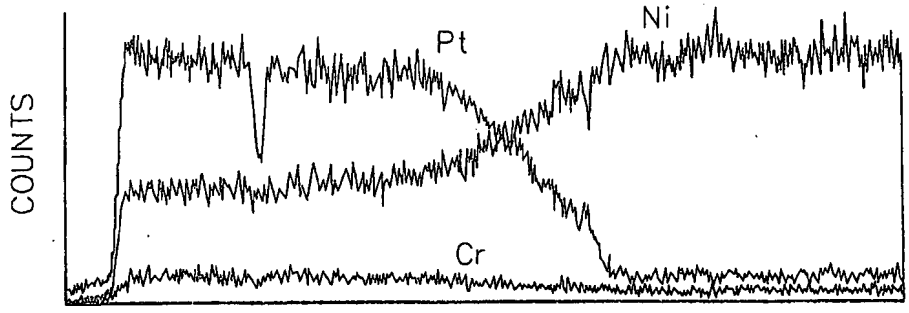

FIG. 8B

FedEx Express

From: Origin ID: ZSYA (480)385-5060
Cindy Kwacala
Ingrassia, Fisher & Lorenz
7010 E. Cochise Road
Scottsdale, AZ 85253

BILL SENDER

SHIP TO: 4803855060
Cindy Kwacala
INGRASSIA FISHER & LORENZ, P.C
7010 E. Cochise Road
SCOTTSDALE, AZ 85253

Ship Date: 03SEP08
Act Wgt: 1 LB
System#: 5310672/INET8061
Account#: S *********

Delivery Address Bar Code

Ref #

RMA #:
Return Reason:

FedEx RETURNS A1
STANDARD OVERNIGHT

TRK# 7980 0472 4835
0221

85253
AZ-US
PHX

98 ZSYA

Align Bottom of Peel and Stick Airbill or Pouch

TO EXPOSE ADHESIVE REMOVE LINER

Missy Hale

From: TrackingUpdates@fedex.com
Sent: Wednesday, September 17, 2008 6:36 AM
To: Missy Hale
Subject: FedEx Delivery Exception

This tracking update has been requested by:

Company Name:	INGRASSIA FISHER & LORENZ, P.C
Name:	Cindy Kwacala
E-mail:	'not provided by requestor'

FedEx attempted, but was unable to complete delivery of the following shipment:

Reference:	002.3315
Ship (P/U) date:	Sep 3, 2008
Estimated delivery:	Sep 12, 2008
Service type:	FedEx International Economy
Packaging type:	FedEx Envelope
Number of pieces:	1
Weight:	0.70 lb.
Special handling/Services	Deliver Weekday

Tracking number: 799899076842

Reason Delivery Not Completed	Recommended Action
1. Unable to deliver shipment, returned to shipper	No action is required. The package is being returned to the shipper.

Please do not respond to this message. This email was sent from an unattended mailbox. This report was generated at approximately 8:35 AM CDT on 09/17/2008.

To learn more about FedEx Express, please visit our website at fedex.com.

All weights are estimated.

Estimated Delivery displayed above is not valid for Money-Back Guarantee or delay claim purposes. Shipments delayed because of Customs or other regulatory delays are not subject to refund or credit under FedEx Money-Back Guarantee Policy. Please see FedEx Service Guide for terms and conditions of service, including FedEx Money-Back Guarantee. For more information, please contact your FedEx Customer Support representative.

To track the latest status of your shipment, click on the tracking number above, or visit us at fedex.com.

This tracking update has been sent to you by FedEx on the behalf of the Requestor noted above. FedEx does not validate the authenticity of the requestor and does not validate, guarantee or warrant the authenticity of the request, the requestor's message, or the accuracy of this tracking update. For tracking results and fedex.com's terms of use, go to fedex.com.

Thank you for your business.